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Argon	A	39.94	Nickel	Ni	58.69
Arsenic	As	74.91	Nitrogen	N	14.01
Barium	Ba	137.4	Osmium	Os	190.2
Beryllium	Be	9.02	Oxygen	O	16.00
Bismuth	Bi	209.0	Palladium	Pd	106.7
Boron	B	10.82	Phosphorus	P	30.98
Bromine	Br	79.92	Platinum	Pt	195.2
Cadmium	Cd	112.4	Potassium	K	39.10
Calcium	Ca	40.08	Radium	Ra	226.0
Carbon	C	12.01	Rhodium	Rh	102.9
Cerium	Ce	140.1	Rubidium	Rb	85.48
Cesium	Cs	132.9	Ruthenium	Ru	101.7
Chlorine	Cl	35.46	Selenium	Se	78.96
Chromium	Cr	52.01	Silicon	Si	28.06
Cobalt	Co	58.94	Silver	Ag	107.9
Copper	Cu	63.57	Sodium	Na	23.00
Fluorine	F	19.00	Strontium	Sr	87.63
Gallium	Ga	69.72	Sulphur	S	32.06
Gold	Au	197.2	Tantalum	Ta	180.9
Helium	He	4.003	Tellurium	Te	127.6
Hydrogen	H	1.008	Thallium	Tl	204.4
Indium	In	114.8	Thorium	Th	232.1
Iodine	I	126.9	Tin	Sn	118.7
Iridium	Ir	193.1	Titanium	Ti	47.90
Iron	Fe	55.85	Tungsten	W	183.9
Lead	Pb	207.2	Uranium	U	238.1
Lithium	Li	6.940	Vanadium	V	50.95
Magnesium	Mg	24.32	Zinc	Zn	65.38
Manganese	Mn	54.93	Zirconium	Zr	91.22

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METALLURGICAL PROBLEMS

BY

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Co-author of "Engineering Metallurgy"

SECOND EDITION
THIRD IMPRESSION

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DEDICATED TO THE MEMORY OF
JOSEPH WILLIAM RICHARDS
PIONEER IN METALLURGICAL CALCULATIONS
AN INSPIRING TEACHER
AND
A MAN OF RARE QUALITIES

PREFACE

The purposes in view in preparing the second edition of this book may be included largely in three categories: (1) the desirability of bringing the work up to date both with respect to changes in the fundamental data used in metallurgical calculations and with respect to changes in metallurgical practice; (2) changes dictated by the experience of the author and of others in eleven years' use of the book, particularly with regard to textual clarification, arrangement, and better balance of the problem material; and (3) the desirability of making available new problem material in place of some of that which has been used repeatedly in class instruction over a long period.

The first edition of "A Textbook of Metallurgical Problems" was an outgrowth of Professor Joseph W. Richards's book "Metallurgical Calculations," which was regarded by many as one of the most useful books available to the metallurgical industry. Since Richards's volume was not in a form most suitable for use as a college text, it was then the object of the present author not only to produce a more recent work in the same field as "Metallurgical Calculations," but also to make available a book more adaptable to student use. In this second edition the same objects remain; the title has been shortened to "Metallurgical Problems" both for the sake of brevity and to avoid emphasizing its function as a textbook to the exclusion of a hoped-for usefulness to industry.

The first edition of this book attempted to follow the methods and forms used by Richards to such an extent as to make it relatively easy to use by those accustomed to his book, while at the same time using more recent data, new material in accordance with later practice, and some innovations in harmony with instructional changes made in college departments of chemistry and physics. The same plan is followed in the second edition, but the changes have been carried further, following progress in technical education. For example, free energy and other thermodynamic concepts did not appear in Richards's book, nor was any use made of methods of calculus. These were introduced in the first edition of this book and have been extended in the second edition. Nevertheless, knowledge of higher mathematics is still relatively unimportant in the use of the book; also, the substitution of the more familiar heats of reaction for free-energy change has not been abandoned for approximate calculations when these may be properly used. With regard to heats of reaction, a change has been made in this edition to the ΔH concept and notation now so widely adopted in physical chemistry and therefore made familiar to present-day students.

In revising the physical and chemical data in this book, the author has drawn from recently published compilations (acknowledged at the appropriate places) rather than from original sources. These compilations for the most part present data in the forms most often desired in scientific work. In some instances these are not the forms most useful in industry, and much time has been spent by the author in conversion to what seemed to be a more readily usable basis. For example, whereas heat capacities and heats of formation are usually given per mol, in this book heat capacities are given per unit weight (kilogram or pound) and for gases per unit volume (cubic meter or cubic foot); heats of formation are given both per mol and per unit weight.

Although training in methods of calculation does not require precise constants or metallurgical data in accord with modern practice, these are highly desirable for the operating metallurgist and are more satisfying to the engineering student. An effort has been made to make this book up to date in both these respects; it is hoped, too, that the solving of problems employing the practical data of modern processes will add to the educational value of the book as an adjunct to metallurgical instruction by other methods.

The problem material, which has been considerably increased, consists in part of problems carried over from the first edition without change, in part of problems of which the substance has been retained with some changes in data, and in part of entirely new problems. Numerous problems that appeared in the first edition have been omitted.

It is unnecessary to reprint the preface to the first edition, but some extracts from it are given in the following paragraphs.

The value of problem work in the study of the fundamental sciences, such as physics and chemistry, is everywhere recognized. Colleges giving thorough instruction in these subjects require the devotion of a large amount of time to the solution of problems that demonstrate various principles of the science. Likewise, in the field of engineering wide use has been made of the training afforded by the making of calculations pertaining to specific phases of the different engineering branches. In engineering education, indeed, the function of problem work is twofold: it not only serves to demonstrate the principles under study but also develops the ability to use those principles in practical work.

It has seemed that the treatment of the subject should be graded in a book suitable for college use; *i.e.*, that the first parts of the book should be relatively simple, should contain a relatively large amount of explanation, and should have the illustrative examples set forth in considerable detail. As the work progresses and the student gains in experience and understanding, the treatment should become more advanced and the explanatory sections more curtailed. It has not been possible to follow entirely the ideal of gradually increasing difficulty, since the subject has had to be divided along metallurgical lines and these do not coincide with those of relative difficulty. In few, if any, cases can it be said that the metallurgy of any one of the major metals is intrinsically easier or more difficult than that of any other major metal.

Another objective is that of securing a proper balance between the task set for the student and the guidance afforded him in accomplishing it—between the problems set for solution and the amount of explanation or illustration given. This is a difficult question in teaching and is especially so in a course of this kind. Obviously if the textbook reduces the solution of every problem to the question of substituting in the proper formula or provides detailed solutions of problems of all types, which the student can then simply follow as models, the purpose of the problem course is largely defeated. It is only through his own thought and his own effort that the student can really learn anything. On the other hand, the textbook can be of great value in presenting and clarifying the underlying principles and in guiding the student, as well as in the services of stating problems and supplying tables of data wherewith to work them. It may be observed that the plan of an instructional book differs radically from that of a book for the practicing engineer. The latter not only desires all portions of the book to be equally explicit but also wants as many timesaving charts and formulas as possible, whereas for the student these same charts and formulas may be real obstacles in the path of his education. Some, of course, are desirable and even necessary, but often they are used too freely.

The greatest value of a problem course is perhaps that of training in the application of a number of different technical principles to a specific problem—the bringing together, correlating, and applying of principles that the student has learned in perhaps a more or less isolated way in various courses in chemistry, physics, and, to a lesser extent, mathematics and other subjects. This constitutes training in that most important yet difficult process, bridging the gap between theory and practice. It helps to combat an unfortunate tendency which is fostered by our educational system—that of separating knowledge into parts or "courses" and thinking in terms of only one division at a time. The problems are designed to give practice in the application of technical principles, chiefly those of physics and chemistry, and an effort has been made to avoid all problems which require no technical knowledge other than that of arithmetic, even though such problems might be of use in learning about some process in metallurgy.

Many of the problem statements are made up from actual data from metallurgical plants, and often the plant is named in the statement. However, a word of caution is perhaps in order against accepting some of the data too literally. No one should regard these statements as a source of accurate information as to the present practice or equipment of any plant. The author would be glad to have important discrepancies in data called to his attention. But while it is intended that the data shall be truly representative, the problem statements must not be regarded as accurately descriptive.

In the preface to the first edition the author recorded his indebtedness to Joseph W. Richards, with whom he was privileged to have been associated for five years. Appreciation was also accorded to G. A. Roush, who, as well as Professor Richards, had formulated many of the problem statements. Valued criticism of certain chapters by Professor Bradley Stoughton, Wilber E. Harvey, Professor John R. Connelly, and Professor T. H. Hazlehurst, Jr., was also acknowledged. The author desires now to record gratefully the assistance received in the way of criticism or material for the second edition from Professor E. A. Peretti, H. C. Siebert, S. Skowronski, Professor Alfred Stansfield, Professor T. H. Hazlehurst, Jr., and Professor M. C. Stuart.

ALLISON BUTTS.

BETHLEHEM, PA.,
March, 1943.

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METALLURGICAL PROBLEMS

CHAPTER I

QUANTITIES AND UNITS

Man's material progress is largely dependent on his ability to measure things. The measuring process has been applied to a great number and variety of attributes and properties, and science is continually extending the process into new fields and devising new ways of measurement in the older fields. At the same time the process has become well standardized with respect to the things most easily and most commonly measured.

Measurement involves not only a process but also a means of expression. The measuring process is essentially one of comparison; the best expression of its result involves the use of a standard unit. Thus, the inch may be taken as a unit and the length of a body determined by comparing it with the standard inch, the result being expressed as so many inches. Unfortunately the adoption of standards, particularly outside the field of science, has varied greatly as regards units in different parts of the world. International agreements, however, have fixed the relative values of many different units and ensured the comparability of our principal measurements.

In measuring the length of a body, for example, there is placed alongside of it a suitably divided standard rule which in its manufacture was compared with another standard of high reliability; this standard in turn was compared with another, the comparison ultimately going back to the standard meter bar kept in the vault of the International Bureau of Weights and Measures at Sèvres, France, or the standard yard bar kept at the Standards Office in London.

The weight and the mass of a body are determined by a similar ultimate comparison with an internationally recognized standard block having a mass of 1 kilogram or another standard block having a mass of 1 pound. The *mass* of a body is defined as the quantity of matter in it, or the property that causes it to possess inertia; it does not vary with the location or position of the body. The *weight* of a body is the force with which it is attracted toward the center of the earth by gravity; it may vary with location. Mass and weight, being different physical entities, require different units, though unfortunately certain of these units for mass and weight have the same name, as pound mass and pound weight or gram mass and gram weight. Since a weight of 1 pound is the force exerted by the earth on a 1-pound mass, the term "weight" is often used in ordinary language where "mass" is meant; but no confusion need arise if it is remembered that the mass of a body is an unvarying quantity of matter while the weight of the body is the force exerted on it by the earth. Variation in the weight of a body between one point and another on the earth's surface is too small to require consideration in commercial transactions or industrial operations.

In making technical calculations one must select the units most suited to his purpose. A choice must be made between two systems or groupings of units. One of these has the advantage of wider general and commercial use among English-speaking peoples and, therefore, of being more intelligible to them in the light of their common experience. The other has the advantage of a more logical basis and simpler relations between different members within the system and also of broader international and scientific use. This latter, the metric system, will be given general preference in this book because of its simpler basis, because the student has become accustomed to it in his prerequisite study in chemical calculations, and because it often facilitates calculations in metallurgy, making them more rapid and less liable to mechanical error. However, since the English system is customarily used outside the laboratory in the plant operations and engineering practice of all the English-speaking countries, in both metallurgical engineering and the other branches, it is desirable for the student to have some practice in using this system also in metallurgical calculations. Accordingly many of the problems in this book will be stated in English units and results required in the same terms. In some cases conversion of units from one system to the other will be desirable, either because the data are given partly in one system and partly in the other or because the computations may be facilitated. Conversion tables are given beginning on pages 427 and 430.

Magnitude of Units.—In calculations in chemistry the student will have been accustomed to the use of the laboratory units—grams, cubic centimeters, liters, etc. These units are too small for convenience in industrial practice, except in certain cases. In general the problems in this book will represent actual operating conditions, frequently using data from metallurgical plants. Accordingly units of suitable size will be employed, as kilograms, metric tons, cubic meters. No difficulty will be caused, because of the simple relation between the smaller and the larger units. The kilogram equals 1,000 grams, the metric ton equals 1,000 kilograms, the cubic meter equals 1,000 liters or 1,000,000 cubic centimeters. Of particular importance is the fact that there is the same relation between kilograms and cubic meters as between grams and liters; the law stating that one molecular weight of a gas in grams occupies 22.4 liters at standard conditions means also that one molecular weight in kilograms occupies 22.4 cubic meters. For example:

32 g. of oxygen occupies 22.4 liters at standard conditions.

Therefore:

32 kg. of oxygen occupies 22.4 cu. m. at standard conditions.

Likewise we shall use as the unit of heat in most cases the kilogram calorie (or "large calorie," abbreviated Cal.) rather than the gram-calorie (or "small calorie," abbreviated cal.). If 1 gram of carbon yields on combustion 8,100 calories then 1 kilogram yields 8,100 Calories.

Some Important Units and Definitions.—The liter is regarded as the fundamental metric unit for measurement of volume of liquids, and it has become customary to express small liquid volumes in milliliters (thousandths of a liter) rather than in cubic centimeters. The *liter* was originally defined as the volume occupied by the amount of pure water having a mass of 1 kilogram at the temperature of maximum density, 4°C., whereas the *cubic centimeter* is defined in terms of the standard meter of length. Originally no distinction was made between the milliliter and the cubic centimeter, and for ordinary practical purposes these two units are equal. Precise measurements have determined that 1 ml. = 1.000027 cc.; while this numerical difference is negligible for the purpose of this book, so that we may assume that 1,000 liters = 1 cu. m., we shall follow the present custom of expressing small volumes of liquids in milliliters.

The *density* of a body or substance is its mass per unit volume. The units in which it is expressed are not specified in its definition, and its numerical value will depend on the units used. In the metric system it is usually expressed in grams per cubic centimeter (or per milliliter for liquids). The *specific gravity* of a solid or liquid body is the ratio of its mass to the mass of an equal volume of water at the temperature of maximum density. Specific gravity is thus a pure number; and when density is expressed in the common metric units, the density and the specific gravity are equal. (The specific gravity of gases, however, is often referred to air at standard conditions, instead of to water, as unity.) In suitable units, density may be taken as weight per unit volume.

Specific volume is the reciprocal of density, *i.e.*, specific volume is volume per unit mass, and its numerical value will also depend upon the units used.

Discussion of the several comprehensive systems of units lies outside the scope of this book; nor will it be necessary to detail the various units used in the fields of mechanics, electricity and magnetism, etc. Some of these will be defined at the appropriate place in later chapters, but for the most part we shall have occasion to use only the more common units concerning which there should be no confusion. Since most metallurgical work is done at high temperatures, however, it will be well to review at this point the common heat units and their relations to units of energy and power. Some heat units are discussed further in Chaps. III, V, and XXI.

Thermal Units.—Thermal measurements must be considered from two standpoints, (1) that of *quantity* of heat energy and (2) that of *temperature.* The temperature of a body is defined on the basis of its ability to yield heat to another body or the surroundings (at lower temperature) or receive heat from another body or the surroundings (at higher temperature); it is expressed in degrees centigrade, Fahrenheit, etc. Knowledge of the temperature scales by the student is here assumed. Quantity of heat is defined in terms of energy. The common unit of heat quantity in the metric system is the *calorie,* defined as $\frac{1}{860}$ watt-hour. In the English system there is used the *British thermal unit* (B.t.u.), defined as 251.996 calories. The relations from which these values were originally derived, although not exact, are often useful, *viz.:* the calorie is equal to the quantity of heat required to raise the temperature of 1 gram of water 1 degree centigrade, and the B.t.u. is equal to the quantity of heat required to raise the temperature of 1 pound of water 1 degree Fahrenheit. Since these quantities vary slightly over the temperature scale, it is necessary, for precision, to specify the exact point of temperature change of the water; this is usually taken as 15 to 16°C. because this corresponds with the average over the range 0 to 100°C.

In mechanics the general unit of energy is the *erg,* defined as the work done by a force of 1 dyne exerted through a distance of 1 centimeter. This small unit will not be used in this book, but its multiple the *joule,* which equals 10^7 ergs, will be used as a unit of either mechanical energy or heat energy.

4.186 joules = 1 cal.; 1,054.9 joules = 1 B.t.u.; 778.26 joules = 1 ft.-lb.

The *watt* is defined as the expenditure of 1 joule of energy per second.

Power is energy per unit of time. Thus, calories per second, B.t.u. per second, and foot-pounds per second are all units of power. A joule per second is the same as a watt, so that

4.186 watts = 1 cal. per second, and 4.186 kw. = 1 Cal. per second.

The *specific heat* of a substance is defined as the quantity of heat required to raise the temperature of one unit of it 1 degree. It is also called the *heat capacity.* It is commonly expressed in calories per gram of substance per degree centigrade. The specific heats of gases are often given in calories per liter (= Calories per cubic meter) at standard conditions per degree centigrade instead of on the weight basis. The heat capacity of a mol of substance, called *molal heat capacity,* is often useful; this is equal to the specific heat multiplied by the molecular weight. The molal heat capacity of a gas is equal to its volumetric specific heat (per liter) multiplied by 22.4, since the gram-molecular weight occupies 22.4 liters at standard conditions.

Specific heats of substances vary with temperature, the amount of variation being small over a small range of temperature, such as one of less than 100°C., but of considerable importance over the large temperature ranges encountered in metallurgical work. These variations with temperature, as well as the calculation of the total heat contents of bodies and of volumes of gases, are discussed in Chaps. III and V.

Summary.—Some of the units and relations already given are summarized below, and a number of others of importance are added so that the student may refresh his memory of them and have them available for convenient reference. Reference may also be made to the conversion table (Table LIV, page 427).

1 ml. or 1 cc. of water weighs 1 g (almost exactly at 4°C.; approximately at other temperatures up to 100°C)

1 cc. of any other substance weighs the number of grams equal to its density or specific gravity.

1 liter of water weighs 1 kg. at ordinary temperatures.

1 cu. ft. of water weighs 62.4 lb. at ordinary temperatures.

1 metric ton = 1,000 kg. = 2,205 lb. (It will be noted that the metric ton is only about 10 per cent larger than the common short ton of 2,000 lb. and 1.5 per cent smaller than the English long ton of 2,240 lb.)

1 Cal. is approximately equal to the quantity of heat required to raise the temperature of 1 kg. of water 1°C. (Varies at different temperatures—a negligible variation for most purposes for temperatures below 100°C.)

1 B.t.u. (British thermal unit) is approximately equal to the quantity of heat required to raise the temperature of 1 lb. of water 1°F.

1 Cal. = 3.97 B.t.u. 1 B.t.u. = 0.252 Cal. = 252 cal

The volume of a gas expands $\frac{1}{273}$ of its volume at 0°C. for each rise of 1°C. (pressure remaining constant); or the volume of a gas expands $\frac{1}{492}$ of its volume at 0°F. for each rise of 1°F. (pressure remaining constant). (While these relations, from Charles's law, hold strictly only for a perfect gas, they are regularly used for all gases.) Absolute zero is −273°C., or −460°F. (The more precise values are −273.16°C. and −459.69°F.)

The volume of a gas varies inversely with the pressure, temperature being constant (Boyle's law).

"Standard conditions" for gases are a temperature of 0°C. and pressure equal to that of a column of mercury 760 mm. in height.

1 watt = 1 amp. × 1 volt. 1 kw. = 1,000 watts.

1 joule = 1 watt-sec. 4.186 joules = 1 cal.

860 Cal. per hour = 1 kw., or 860 cal. per hour = 1 watt.

0.239 cal. per second = 1 watt. 746 watts = 1 hp.

1 hp. = 33,000 ft.-lb. per minute.

1 kw. = 102 kg.-m. per second.

Normal atmospheric pressure = 14.70 lb. per square inch = 10,333 kg. per square meter.

Precision of Metallurgical Calculations.—Since the problems in this book are for the most part based on practical operating conditions, they should be solved with a precision appropriate to such conditions—neither greater nor less. Carrying out results to five or six figures not only is a needless waste of time but may be misleading and is generally bad practice. Three or four significant figures should be the rule; this number usually not only is all that is justified in view of the precision of available data, but is sufficient also to allow for the fact that in cases of doubt it is better to err on the side of too great precision rather than too little. This number corresponds with the precision of the 10-in. slide rule.[1]

In using atomic weights, it is in most cases desirable to use the round numbers, as 64 for Cu, 56 for Fe, etc. In some cases the more precise figures should be used.

The statement that a piece of metal weighs 10.40 kg. should carry with it the implication that the piece has been weighed to an accuracy of one-hundredth of a kilogram. If weighed to only one-tenth of a kilogram, the weight should be stated as 10.4 kg., since it is not known whether the next figure would be 0 or some other figure. If weighed to one-thousandth of a kilogram, another figure would be known but need not be stated if the purpose in view does not require a precision of more than four significant figures.

Usually metallurgical data are not sufficiently precise to justify the use of more than three or four figures, particularly in the rougher operations of ore treatment. Given weights are often approximations. Chemical analyses are seldom reliable to more than three figures. Even then their accuracy is dependent on having a proper sample for analysis, and the sample may be even less reliable. Chemical reactions used in calculations do not always accurately represent what occurs. The presence of impurities is disregarded. Assumptions are usually necessary, either for simplification or because of lack of information. Such considerations as these serve to indicate the impracticability of greater precision. Some types of operation, of course, permit of a much greater precision than others. Calculations are essentially an application of theory to practice; the more experience one has in applying them in practice, the better is he able to judge of the suitable precision in particular cases and, in general, the more he realizes the lack of exactness in the usual case. At the same time, the value of calculations and their indispensability for design, control, and improvement in operation become more evident. The impracticability of great precision in figures must not be used as an excuse for lack of precision in thought and in method.

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[1] But little practice with the slide rule is required to make its use easy, rapid, and accurate. It is recommended for metallurgical calculations; in fact, its use is practically imperative for the student if the problems given at examination time are to be completed in the time allotted.

CHAPTER II

THE CHEMICAL EQUATION

The chemical equation expresses by means of symbols what occurs when a chemical reaction takes place. It shows not only what substances react or are formed but also the actual *relative quantities* of each. The equation gives the number of atoms or molecules of each substance reacting, and the amount of each substance corresponding to the atomic quantities indicated may be expressed in any units desired, either by weight or by volume; the truth of the equation is not altered by the substitution of one unit for another so long as the relative quantities involved are not changed. Thus, the equation written

$$2H_2 + O_2 = 2H_2O$$

means that 4 parts of hydrogen (by weight) react or combine with 32 parts of oxygen (by weight) to form 36 parts of water (by weight), where for "parts" we may read grams, kilograms, pounds, or any other *weight* unit, as long as each term of the equation is expressed in the same unit. The same equation likewise means that 2 parts of hydrogen (by volume) react or combine with 1 part of oxygen (by volume) to form 2 parts of water vapor (by volume), where for "parts" we may read liters, cubic meters, cubic feet, or any other *volume* unit, as long as each term of the equation is expressed in the same unit.

It is likewise permissible, and often very useful, to express some of the terms gravimetrically and some volumetrically. For example, it may be desired to find the number of *liters* of oxygen necessary to burn 100 *grams* of hydrogen. The term $2H_2$ would then be interpreted as 4 grams, but the term O_2, instead of being assigned a value of 32 grams, would be given the value 22.4 liters. The symbol O_2 in the equation means a molecular quantity of oxygen: When expressed in grams it is a gram-molecular weight, or 32 grams. When expressed in liters it is a molecular volume, or 22.4 liters at standard conditions of temperature and pressure. The above equation, then, may be interpreted to mean that 4 grams of hydrogen combines with 22.4 liters of oxygen to form 44.8 liters of water vapor.

It will be noted that, when the equation is used in this manner, care must be taken to see that the equation is written in molecular terms. Since the molecule of oxygen contains two atoms, the oxygen must be expressed in the equation as O_2, which is equivalent to 22.4 liters. The chemical law here applied is as follows:

A gram-molecular weight of any gas occupies 22.4 liters at standard conditions, or **a kilogram-molecular weight of any gas occupies 22.4 cubic meters at standard conditions.**

The following example illustrates the use of the chemical equation in this manner:

Example 1

A Bessemer steel converter is charged with 10,000 kg. of molten iron containing 4.0 per cent carbon, 1.5 silicon, and 1.0 manganese. The impurities are oxidized and removed from the iron by blowing air into the converter. One-quarter of the carbon is oxidized to CO_2 and three-quarters to CO.

Required: The total volume of air necessary, in cubic meters.

Solution: The reactions are:[1]

$$C + O_2 = CO_2. \tag{1}$$
$$2C + O_2 = 2CO. \tag{2}$$
$$Si + O_2 = SiO_2. \tag{3}$$
$$2Mn + O_2 = 2MnO. \tag{4}$$

The required volume of oxygen, as shown by the equations, will first be calculated. In using the equations it will be convenient to place the atomic or molecular quantities over the respective symbols, thus:

$$\overset{12}{C} + \overset{22.4}{O_2} = CO_2. \tag{1}$$
$$\overset{2 \times 12}{2C} + \overset{22.4}{O_2} = 2CO. \tag{2}$$
$$\overset{28}{Si} + \overset{22.4}{O_2} = SiO_2. \tag{3}$$
$$\overset{2 \times 55}{2Mn} + \overset{22.4}{O_2} = 2MnO. \tag{4}$$

(For the sake of simplicity, in the remainder of this book the atomic or molecular quantities will not be placed over the symbols in equations; the student, however, may often find it desirable to do so in his work, particularly until he has gained experience.)

There is contained in the pig iron $0.04 \times 10{,}000 = 400$ kg. of C, of which 100 kg. goes to CO_2 and 300 kg. to CO. The amount of Si oxidized is 150 kg. and of Mn 100 kg.

Equation (1) means that 12 kg. of C requires 22.4 cu. m. of O_2 to form CO_2, or:

$$1 \text{ kg. of C requires } \frac{22.4}{12} \text{ cu. m. of } O_2.$$

The 100 kg. of C therefore requires $100 \times \frac{22.4}{12} = 187$ cu. m. of O_2.

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[1] The student will find it desirable to form the habit of setting down any reactions that are to be used as the first step, or one of the first steps, in the solution of any problem. With the reactions before one, the reasoning of the solution is simpler and there is less likelihood of error in computation.

Likewise, reaction (2) means that 24 kg. of C requires 22.4 cu. m. of O_2 to form CO, so that:

$$300 \text{ kg. of C requires } 300 \times \frac{22.4}{24} = 280 \text{ cu. m. of } O_2.$$

Similarly, since the atomic weight of Si is 28, 150 kg. of Si requires $150 \times \frac{22.4}{28} =$ 120 cu. m. of O_2, and 100 kg. of Mn requires $100 \times \frac{22.4}{110} = 20$ cu. m. of O_2.

By adding it is found that the total oxygen required is $187 + 280 + 120 + 20 =$ 607 cu. m. of O_2.

Since air is 21.0 per cent O_2 by volume, the volume of air required is $\frac{607}{0.21} = 2{,}890$ cu. m.

(This is the volume at standard conditions of temperature and pressure, since the solution has depended on use of the factor 22.4, which is the molecular volume at standard conditions.)

The molecular quantity of a substance is often designated by the term "mol." By weight, the mol is the same as the gram-molecular weight; the terms "kilogram-mol" or "pound-mol" may be used to designate a molecular weight in kilograms or pounds. By volume, a mol of gas represents 22.4 liters at standard conditions.

The consideration or calculation of quantities by mols instead of by grams, liters, pounds, etc., is sometimes referred to as the "mol method." This method has many advantages. The mol is the natural combining unit in chemistry. In the above illustration of the combination of hydrogen and oxygen to form water vapor, it is noted that the relative *volumes* are the same as the relative number of mols. The student will find this the simplest way of handling reactions in which gases are involved.

Volume-weight Relations in the English System.—Finding the volume of a gas corresponding to a given weight, or vice versa, may be done with equal facility in the English system of units by use of the constant 359 instead of 22.4. The relation here is:

A pound-molecular weight of any gas occupies 359 cu. ft. at standard conditions.

For example, the volume of 10 lb. of oxygen is $10 \times {}^{359}/_{32} = 112$ cu. ft. at standard conditions. The reference standard here is the same as in the metric system, *viz.*, 0°C. and 760 mm. of mercury, equivalent in English units to 32°F. and 29.92 in. of mercury.

A chance relation, sometimes useful in computing in the English system, is that a molecular weight of a gas in ounces (or ounce-mol) occupies approximately 22.4 cu. ft. at standard conditions. In other words, there is approximately the same numerical relation between ounces and kilograms as between cubic feet and cubic meters. The closeness of the approximation can be seen from the fact that the number of ounces (avoirdupois) equivalent to a kilogram is 35.27 and the number of cubic feet equivalent to a cubic meter is 35.31.

Problems

1. A copper converter receives a charge of 60 metric tons of matte containing 54 per cent FeS. The FeS is oxidized by blowing air into the converter according to the reaction

$$2FeS + 3O_2 = 2FeO + 2SO_2.$$

Air is 21.0 per cent oxygen by volume. A metric ton is 1,000 kg.

Required: 1. The total volume of air necessary, in cubic meters.

2. The volume of SO_2 formed.

3. The number of kilograms of FeO formed.

4. The weight of slag formed, in metric tons, if the FeO constitutes 65 per cent of the slag.

2. Iron oxide is reduced to iron in an electric furnace in accordance with the following reaction:

$$4Fe_2O_3 + 9C = 8Fe + 6CO + 3CO_2.$$

Required: 1. The number of kilograms of Fe_2O_3 which must be reduced to make 1 metric ton of Fe.

2. The number of kilograms of carbon required.

3. The number of cubic meters of CO and of CO_2 produced at standard conditions.

4. The number of kilograms of CO and of CO_2 produced.

3. A charge in a zinc retort yields 50 lb. of zinc. The charge consists of ore containing 56 per cent ZnO, 44 per cent gangue, and coal containing 90 per cent carbon, 10 per cent ash. The reduction takes place in accordance with the reaction

$$ZnO + C = Zn + CO.$$

Enough coal is used to furnish five times as much carbon as the equation demands.

Required: 1. The weight of ore in the charge, in pounds.

2. The percentage of coal in the charge.

3. The volume of CO evolved, in cubic feet.

4. Lead is reduced from galena (PbS) in an ore hearth by reaction of PbS with PbO in one reaction and of PbS with $PbSO_4$ in another reaction, Pb and SO_2 being formed in both cases. Three times as much Pb is produced by the PbO reaction as by the $PbSO_4$ reaction, the two reactions taking place simultaneously.

The weight of PbS reduced in the two reactions together is 6,600 kg.

Required: 1. The total weight of lead resulting from the reactions and the weight (kilograms) and volume (cubic meters) of SO_2 produced.

2. The percentage of PbO and of $PbSO_4$ contained in the PbS-PbO-$PbSO_4$ mixture.

5. A copper ore contains 6 per cent Cu and 35 per cent S. The copper mineral is chalcopyrite ($CuFeS_2$), and S is also present as iron pyrite (FeS_2). The rest of the ore is gangue containing no Cu, S, or Fe.

The ore is roasted until all the sulphur is removed, the following reactions taking place:

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2.$$
$$4CuFeS_2 + 13O_2 = 4CuO + 2Fe_2O_3 + 8SO_2.$$

The amount of oxygen supplied to the furnace (contained in air) is 200 per cent n excess of the amount demanded by the equations.

Required: 1. The number of pounds of each of the above minerals and of the gangue contained in 1 short ton of ore.

2. The cubic feet of oxygen required by the equation in roasting 1 ton of ore.

3. The cubic feet of air actually supplied, per ton of ore.

4. The total weight of Fe_2O_3 and the total volume of SO_2 produced in roasting 1 ton of ore.

6. Aluminum is produced by electrolytic decomposition of Al_2O_3, using a carbon anode. The oxygen set free when the Al_2O_3 is decomposed combines with carbon at the anode. Assume that 85 per cent of the oxygen forms CO, 15 per cent CO_2. The daily output of one cell is 400 lb. of aluminum

Required: 1. The chemical reaction occurring, balanced with minimum whole numbers.

2. The pounds of Al_2O_3 consumed per day in each cell.

3. The cubic feet of CO and CO_2 liberated, per day.

7. Sulphur contained in steel as FeS is removed therefrom in an electric furnace by the addition of lime and ferrosilicon, the following reaction taking place:

$$2CaO + 2FeS + Fe_xSi = SiO_2 + 2CaS + (x + 2)Fe,$$

n which the ferrosilicon is represented by Fe_xSi.

Required: 1. If the ferrosilicon contains 50 per cent Fe and 50 per cent Si, what value of x in the formula Fe_xSi would represent its composition?

2 How many pounds of lime and how many pounds of this ferrosilicon would be required to remove 100 lb. of sulphur?

8. In an iron blast furnace, hematite (Fe_2O_3) is reduced by carbon monoxide, which is formed by combustion of carbon in the coke by means of the air blast The conditions of chemical equilibrium require that there be an excess of CO present in order to make the reduction equation proceed from left to right The equation may be represented as follows:

$$Fe_2O_3 + xCO = 2Fe + 3CO_2 + (x - 3)CO.$$

In a certain blast furnace the ratio of $CO:CO_2$ in the products of the above reaction was 1.8:1 by volume. The furnace reduced 800 metric tons of iron (Fe) per day.

Required: 1 The equation representing the reduction with CO and CO_2 formed in the ratio 1.8:1, balanced with minimum whole numbers.

2 The cubic meters of CO and of CO_2 produced per day

3. The theoretical consumption of coke, per metric ton of iron reduced, assuming the coke to be 90 per cent carbon

4. The cubic meters of blast (air) necessary for combustion of the carbon in the coke to CO, per ton of iron reduced.

5. If there is charged to the furnace one-fifth as much limestone ($CaCO_3$) as the amount of Fe_2O_3 reduced, what will be the actual ratio of CO to CO_2 in the furnace gases after adding the CO_2 resulting from decomposition of $CaCO_3$ into CaO and CO_2?

9. A zinc retort is charged with 70 kg. of roasted zinc concentrates carrying 45 per cent zinc, present as ZnO. Reduction takes place according to the reaction

$$ZnO + C = Zn + CO.$$

One-fifth of the ZnO remains unreduced. The zinc vapor and CO pass into a condenser, from which the CO escapes and burns to CO_2 as it emerges from the mouth of the condenser. The CO enters the condenser at 300°C. and 700 mm pressure.

Required: 1. The volume of CO in cubic meters entering the condenser (*a*) measured at standard conditions and (*b*) measured at the actual conditions (see p. 20).

2. The weight of CO, in kilograms.

3. The volume of CO_2 formed when the CO burns, measured at its temperature of 750°C., pressure of 765 mm.

4. The volume (standard conditions) and weight of air used in burning the CO (see p. 18).

CHAPTER III

COMBUSTION

Metallurgical treatments are usually performed at high temperatures. Though electric furnaces are sometimes employed for such operations as smelting, refining, melting for casting, and heat-treating, combustion of a fuel is much more commonly employed to supply the necessary heat for these and many other processes. Consequently the subject of fuels and combustion is of vital interest to the metallurgist and is usually included in the study of general or introductory metallurgy. The quantitative study of combustion, which constitutes the topic of this chapter, is of great value both theoretically and practically. It deals first with the amount of air required for combustion and the volume and composition of the gases resulting; a knowledge of these is necessary in the design of furnaces and in getting maximum efficiency in the use of a given fuel. Thousands of dollars may be wasted annually, for example, in the operation of an open-hearth steel furnace if either too much or too little air is used in combustion. The loss of heat from a furnace through being carried out in the hot gases can be readily calculated, and through this and other factors the thermal efficiency of a furnace or a process can be computed and studied. Likewise the temperature attained in combustion of a given fuel can be calculated both for theoretical and actual conditions.

The principles of calculation used in working combustion problems are fundamental and also for the most part relatively simple. Consequently the problems in this chapter form a desirable introduction to and preparation for the more strictly metallurgical problems of the later chapters. A thorough understanding by the student of the principles in this chapter is essential as a foundation for the work which follows.

Combustion of a fuel consists in the chemical combination of the oxidizable elements of the fuel with the oxygen of the air. In the ordinary heat-giving process the aim is to burn the fuel as fully as possible so as to produce the maximum amount of heat. The carbon of the fuel will be mostly burned to CO_2; for the present we may neglect formation of CO, which represents only a partial combustion. Consider first a coal that has been analyzed quantitatively and found to contain:

	Per Cent		Per Cent
C	72	N	1
H	4	H_2O	3
O	8	Ash	12

In general the analysis of solids and liquids is made by weight and that of gases by volume, and their percentage compositions are ordinarily stated correspondingly. **Throughout this book, except when specifically stated otherwise, the analyses of solid and liquid materials will be given in percentage by weight, and the analysis of gases in percentage by volume.**

Let it be required to find the cubic meters of air (at standard conditions) theoretically necessary to burn 1 kg. of the above coal completely.

The reactions occurring in the combustion are:

$$C + O_2 = CO_2. \qquad (1)$$

$$2H_2 + O_2 = 2H_2O. \qquad (2)$$

Ash, H_2O, and N, of course, do not burn (oxidize), and the O contained in the coal goes to supply part of the oxygen needed in the equations, thus reducing the amount to be supplied by air.

1 kg. of coal contains 0.72 kg. of C and 0.04 kg. of H.

From Eq. (1): 0.72 kg. of C requires $0.72 \times {}^{32}\!/_{12}$ = 1.92 kg. of O
From Eq. (2): 0.04 kg. of H requires $0.04 \times {}^{32}\!/_{4}$ = 0.32
Total O required = 2.24 kg.
O present in coal = 0.08
O to be supplied by air = 2.16 kg

Air is 23.2 per cent O by weight

The weight of air required is, therefore, $\frac{2.16}{0.232} = 9.31$ kg

1 cu. m. of air weighs 1.293 kg at standard conditions.

The volume of air required is, therefore, $\frac{9.31}{1.293} = 7.20$ cu. m.

In this solution the air has been found by weight and in the last step converted to volume. It is usually preferable, however, to find the volume directly, since it simplifies the calculation of the flue gases. The solution by this method is as follows:

From Eq. (1): 0.72 kg. of C requires $0.72 \times \frac{22.4}{12}$ = 1.344 cu. m. of O_2
0.04 kg. of H requires $0.04 \times \frac{22.4}{4}$ = 0.224
Total O_2 required = 1.568 cu. m.
O_2 present in coal = 0.08 kg. $\times \frac{22.4}{32}$ = 0.056
O_2 to be supplied by air = 1.512 cu. m.

Air is 21.0 per cent O_2 by volume.

The volume of air required is, therefore, $\frac{1.512}{0.21} = 7.20$ cu. m.

In the latter solution it will be observed that it has been necessary to convert the given weight of oxygen (0.08 kg.) to cubic meters in order to subtract it in finding the amount to be supplied by air. This operation of changing from weight to volume of a gas or, conversely, that of finding the weight of a certain volume of a gas is one that has to be employed frequently in metallurgical problems. The method of doing it here, which will be used throughout this book, follows directly from the law that the molecular weight of a gas in kilograms occupies 22.4 cu. m. at standard conditions. Stated in words, the kilograms of the gas multiplied by 22.4 divided by the molecular weight of the gas gives the cubic meters of the gas. Or, briefly:

$$\text{Vol. in cu. m} = \text{wt in kg} \times \frac{22.4}{\text{mol. wt}},$$

and

$$\text{Wt. in kg.} = \text{vol. in cu. m.} \times \frac{\text{mol wt.}}{22.4}.$$

This method has the advantage of being readily used for all gases if only the molecular weight is known. If great precision is required, it should not be used because the factor 22.4 varies slightly for different gases. Instead, the actual weight of a cubic meter of various gases may be obtained from a reference table. The weight of a cubic meter of any gas is also approximately equal to one-half its molecular weight × 0.09 kg., a relation which follows from the fact that 1 cu. m. of hydrogen weighs 0.09 kg. and the molecular weight of hydrogen is approximately 2. This may be stated:

$$\text{Wt. in kg.} = \text{vol in cu. m} \times \frac{\text{mol. wt.}}{2} \times 0.09.$$

NOTE: The solution of almost every metallurgical problem presents a choice of steps: there are a number of paths to the goal. The student should be advised as to the shorter or more logical method when there is a distinct preference but in general should be allowed to make his own choice The superior student will for his own benefit become acquainted with different methods and use each of them enough to ensure thorough understanding

Table I, page 16, shows actual determined weights of common gases and also calculated weights for comparison.

Let it now be required to find the volume and percentage composition of the gases resulting from the combustion of 1 kg. of the coal of which the analysis has been given. The resulting gases should be interpreted to mean not only the gases found in reactions (1) and (2) but also the gasified nitrogen and H_2O from the coal and the nitrogen introduced by the air—*i.e.*, *all* the gases which would be present in the furnace just beyond the point of combustion. Practically, these gases are intermixed, and it is the entire mixture with which we are concerned. The mixture is variously termed "the flue gases," "the chimney gases," "the

TABLE I.—WEIGHTS OF GASES
(In kilograms per cubic meter, or grams per liter, at 0°C., 760 mm.)

Gas	Formula	Weight, measured	Weight, calculated from molal volume of 22.4
Acetylene	C_2H_2	1.173	1.161
Air	.....	1.293	1.292*
Ammonia	NH_3	0.771	0.760
Benzene	C_6H_6	3.582	3.484
Carbon dioxide	CO_2	1.977	1.964
Carbon monoxide	CO	1.250	1.250
Chlorine	Cl_2	3.214	3.166
Ethane	C_2H_6	1.357	1.341
Ethylene	C_2H_4	1.260	1.251
Fluorine	F_2	1.696	1.696
Helium	He	0.1782	0.1787
Hydrochloric acid	HCl	1.639	1.628
Hydrogen	H_2	0.0900	0.0900
Hydrogen sulphide	H_2S	1.539	1.522
Mercury vapor	Hg	9.021	8.956
Methane	CH_4	0.717	0.716
Nitrogen	N_2	1.251	1.251
Oxygen	O_2	1.429	1.429
Sulphur dioxide	SO_2	2.927	2.860
Water vapor	H_2O	0.8063	0.8042

* Assuming 23.2 per cent oxygen and 76.8 per cent nitrogen by weight.

products of combustion," etc. The last term is often used, and it should be noted that it includes much more than the gases formed in the chemical reactions of combustion; it includes all the flue gases. The various possible constituents of the flue gases will be listed later.

From Eq. (1): 0.72 kg. of C forms $0.72 \times \frac{44}{12} = 2.64$ kg. of CO_2.
0.04 kg. of H forms $0.04 \times \frac{36}{4} = 0.36$ kg. of H_2O.
From the coal is obtained directly 0.03 kg. of H_2O
0.01 kg. of N

The air is 76.8 per cent N by weight. From it is obtained:

$$0.768 \times 9.31 = 7.15 \text{ kg. of N.}$$

Summarizing and changing to volume:

$$CO_2 = 2.64 \times \frac{22.4}{44} = 1.34 \text{ cu. m.}$$

$$H_2O = 0.39 \times \frac{22.4}{18} = 0.49$$

$$N_2 = 7.15 \times \frac{22.4}{28} = 5.74$$

$$\text{Total} = \overline{7.57} \text{ cu. m.}$$

Percentage composition:

$$CO_2 = \frac{1.34}{7.57} = 17.7 \text{ per cent}$$
$$H_2O = \frac{0.49}{7.57} = 6.5$$
$$N_2 = \frac{5.74}{7.57} = 75.8$$

The solution of this part can be made more easily by reference to the direct volume method used in finding the air requirement and applying the chemical law, as follows:

When gases react, the combining volumes are in the same ratio as the number of molecules.

This means that in Eq. (1) the volume of CO_2 is equal to the volume of O_2, since there is one molecule of each. In Eq. (2) the volume of H_2O is twice the volume of O_2, since there are two molecules of H_2O to one of O_2.

Hence, directly from the air-requirement solution:

$$\begin{aligned} CO_2 &= 1.344 \text{ cu. m.} \\ H_2O = 2 \times 0.224 &= 0.448 \\ H_2O \text{ from coal } = 0.03 \times \frac{22.4}{18} &= 0.037 \\ N_2 \text{ from coal } = 0.01 \times \frac{22.4}{28} &= 0.008 \\ N_2 \text{ from air } = 0.79 \times 7.20 &= \underline{5.688} \\ \text{Total} &= 7.525 \text{ cu m.} \end{aligned}$$

A good way to obtain the amount of nitrogen from the air is by subtracting the amount of oxygen from the amount of air. Thus, above:

By weight: $N = 9.31 - 2.16 = 7.15$ kg.
By volume: $N_2 = 7.20 - 1.512 = 5.688$ cu m.

Composition of Air.—According to the "International Critical Tables,"[1] dry air at sea level contains by volume 20.99 per cent oxygen, 78.03 nitrogen, 0.94 argon, and 0.04 other gases (chiefly CO_2). For practical purposes it is permissible to count the argon and minor gases as nitrogen. The composition by weight is readily figured from the known weights of the gases contained or from the weight of the oxygen and the experimentally determined weight of 1.293 kg. for 1 cu. m. of dry air at standard conditions. We have:

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[1] Vol. I, p. 393.

Gas	By volume		By weight	
	Per cent	Parts*	Per cent	Parts*
Oxygen	21.0	4	23.2	3
Nitrogen (*et al.*)	79.0	15	76.8	10
Dry air	100 0	19	100.0	13

* Approximately.

It should be understood that the gases are not chemically combined with each other in air; air is simply a mixture of the component gases.

Weight of Air.—Since air is not a single gas but a mixture of gases, it is customary to change from volume to weight, or vice versa, by use of the actual weight of a unit volume of air at standard conditions:

1 cu. m. of air weighs 1.293 kg. at standard conditions.
1 cu. ft. of air weighs 0.0807 lb. at standard conditions.

It is not theoretically correct to speak of the "molecular weight of air"; but for purposes of calculation the weight of 22.4 cu. m. of air in kilograms, or of 359 cu. ft. of air in pounds, may be used with mathematical correctness as though it were a molecular weight. The value is $22.4 \times 1.293 = 28.96$, or $359 \times 0.0807 = 28.97$; hence, 29 is often used. In this book, use of the actual weights given above will be considered preferable.

Moist Air.—All the foregoing discussion applies only to pure dry air. Air as ordinarily obtained directly from the atmosphere for metallurgical purposes, however, is not dry. The amount of moisture contained varies in different localities and on different days in the same locality. It is usually much higher in summer than in winter. It is usually less than 2 per cent but may reach 5 per cent in hot humid weather. In many cases in metallurgy, and particularly in blast-furnace work,[1] the amount of moisture in the air is of great importance. In other cases it may be neglected and the air assumed dry.

The amount of moisture in air may be expressed as so many per cent H_2O. More commonly, however, it is stated in grains per cubic foot or in grams per cubic meter. Care must be taken to note whether the notation refers to the amount of water vapor included in the moist air or the amount carried by a unit of dry air, for example, whether it is expressed in grams per cubic meter of the moist air or per cubic meter of dry air.

Another very common and very useful way of expressing moisture content is according to its partial pressure. If the barometric pressure is, say, 750 mm. of mercury, the gases composing the atmosphere divide this total pressure in proportion to the percentage (by volume) of each present. Thus, if the air contained 2 per cent H_2O, 20.6 O_2, and 77.4 N_2, the partial pressure of the moisture would be 0.02 × 750, or 15.0 mm.; of the oxygen 154.5 mm., and of the nitrogen 580.5 mm. This is an application of Dalton's law of partial pressures (see page 297). Obviously, if the pressure of the moisture in the air is known, its volume can easily be found (assuming that the total pressure is also known or can be taken as standard pressure, 760 mm.).

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[1] See p. 104.

The amount of moisture that can exist as vapor in air or any other mixture of gases is limited. It has a certain maximum value which depends on the temperature of the mixture. Its maximum partial pressure is called the "saturation pressure." If it is attempted to add additional water vapor to an already saturated mixture, the excess water vapor condenses to liquid. Likewise, if the temperature of a saturated mixture be lowered, some of the water vapor condenses. This is what happens when dew falls at night. The higher the temperature, the greater can be the percentage of water vapor contained. Table XXIV, page 401, gives these maximum pressures for different temperatures, expressed in millimeters of mercury.

The actual amount or pressure of moisture present may, of course, be anything less than saturation. The percentage of saturation is often called, in atmospheric data, the "percentage humidity." If the temperature of the air and the percentage humidity are both known, the vapor pressure can be obtained by use of the table and the amount of moisture can be determined.

Example.—In the problem on page 14, the requirement of dry air was calculated as 7.20 cu. m. per kilogram of coal. Suppose now it was given that the temperature of the air was 25°C. and that it was 60 per cent saturated with water vapor, the barometric pressure being 740 mm. From Table XXIV, the maximum pressure of the water vapor at 25°C. is 23.8 mm. The actual pressure then is $0.60 \times 23.8 = 14.3$ mm. The pressure of the dry air is, therefore, $740 - 14.3 = 725.7$. And since the volumes and pressures are in the same ratio, the volume of water vapor is $\frac{14.3}{725.7} \times 7.20 = 0.142$ cu. m. The volume of moist air required is then $7.20 + 0.14 = 7.34$ cu. m. (measured at standard conditions).

In calculating the products of combustion, this 0.14 cu. m. of H_2O would be added to the rest of the H_2O.

Excess Air.—In the problem on page 14, the "theoretical" requirement of air, *i.e.*, the amount corresponding to the chemical reactions, was calculated. In practice it is necessary, in order to ensure complete combustion, to use an excess of air. The amount of excess is best designated as a percentage of the theoretical requirement. Thus, if it were decided to use 40 per cent excess air for the combustion, the volume of excess air would be 0.40 × 7.20 = 2.88 cu. m. The total air used would be 7.20 + 2.88 = 10.08 cu. m. (dry air). The total moist air would be 1.40 × 7.34 = 10.28 cu. m.

In figuring the flue gases, the excess air should be divided into its components (O_2, N_2, and H_2O), and each of these added in. Note that excess air causes free oxygen in the flue gases. Oxygen in the flue gases indicates excess air, and the amount or percentage of excess air used can be calculated from the oxygen content of the flue gases.

The amount of excess air used in practice depends on the type of fuel and the furnace design. It should be minimized; too great an excess means lower temperature attained and wasted heat, carried out of the furnace in the hot flue gases.

Change of Gas Volume with Temperature and Pressure.—Statement of the volume of a gas has no meaning unless the temperature and pressure of the gas are also stated or understood. In order that statements of gas volumes may be comparable and significant, the convention is adopted of referring the measurement to "standard conditions," which in the metric system means 0°C. and 760 mm. pressure. The best practice in metallurgical calculations is to work with volumes referred to standard conditions, changing from the given conditions to standard when the actual conditions are known or, at the end, changing results from standard to given conditions when the volume at given conditions is required.

The laws of change of volume with temperature and pressure are well known and have been stated on page 5. It should be borne in mind that "referring" the measurement to standard conditions does not mean that the conditions have actually changed; if moist air is referred to 0°C., it is not correct to assume that the moisture content must be changed to allow for condensation of water, as would be done if the temperature actually did change.

Example.—To find the actual volume of the dry air, in the example on page 19, at 25°C., 740 mm.:

$$7.20 \times \frac{273 + 25}{273} \times \frac{760}{740} = 8\ 07 \text{ cu. m.}$$

The actual volume of the moist air would be:

$$(7.20 + 0.14) \times \frac{298}{273} \times \frac{760}{740} = 8.24 \text{ cu. m.}$$

Or the volume of the moist air may be found directly from the dry air by subtracting the pressure of the water vapor (found to be 14 3 mm) from the total pressure in the Boyle's law factor, thus:

$$7.20 \times \frac{298}{273} \times \frac{760}{740 - 14.3} = 8.24 \text{ cu. m.}$$

Unburned Carbon in Ashes.—In burning solid fuels there is a residue of ashes, and this will contain some particles of combustible material that have mechanically escaped combustion. The part of the fuel that is noncombustible under any conditions is termed "ash" in the analyses. This is composed largely of SiO_2, often with some Al_2O_3, CaO, and other inorganic matter. The ashes left as residue include this ash plus some combustible matter, which may be taken as carbon, though obviously that assumption is not wholly true. We have, then:

$$\text{Ashes} = \text{ash} + \text{unburned carbon}.$$

From this relation and the percentage of "ash" in the fuel, the amount of unburned carbon may be calculated when the percentage of carbon in the ashes is known. It may often be desired to assume some figure for this percentage and deduct the amount of unburned carbon from the total carbon present, before figuring the theoretical requirement of air for combustion. In this case the term "theoretical requirement" would be interpreted to include the requirement, not for all the carbon in the fuel, but for the amount of carbon which actually burns or is assumed to burn.

Although the distinction between "ashes" and "ash" is somewhat confusing, it is an important one. The student must bear in mind that "ash" is a chemical term for noncombustible material; the ash cannot contain any carbon. The "ashes" are residual matter from the furnace, containing some carbon.

In reading the statement of a problem, care must be taken to note how the carbon content of the ashes is designated. In some cases it is stated that the ashes are (*i.e.*, contain by analysis) so many per cent carbon. In other cases the weight of the ashes is expressed as a percentage of the coal, on the same basis as the percentage of ash, in which case the amount of carbon is obtained by simple subtraction of these two percentages. Occasionally, the amount of unburned carbon may be expressed as a percentage of the original carbon content of the coal instead of as a percentage of the coal itself.

Combustion of Gaseous Fuel.—Since the volumes of combining gases are in the same ratio as the number of molecules indicated in the chemical equation, the calculations of combustion of gases are easily carried out. For example, in the combustion of ethylene we have:

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O.$$

If 50 cu. m. of C_2H_4 is burned, 150 cu. m. of O_2 is used and 100 cu. m. of CO_2 and 100 cu. m. of H_2O are formed.

A good arrangement of the work in this type of problem is shown in the following example, the gas volumes being tabulated as obtained.

Example 2

Natural gas of the Pittsburgh district analyzes as follows:

	Per Cent
CH_4	85
C_2H_4	3
C_6H_6	3
H_2	5
N_2	4

It is burned with 20 per cent excess air. The air is moist, containing 1.5 per cent water vapor.

Required: 1. The cubic meters of dry air theoretically required for combustion of 1 cu. m. of the gas.

2. The volume of moist air used, including the excess.

3. The volume of the products of combustion.

Solution:

	O_2	CO_2	H_2O	N_2
$CH_4 + 2O_2 = CO_2 + 2H_2O$	1.70	0.85	1.70	
$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$	0.09	0.06	0.06	
$C_6H_6 + 7\frac{1}{2}O_2 = 6CO_2 + 3H_2O$	0.225	0.18	0.09	
$2H_2 + O_2 = 2H_2O$	0.025	....	0.05	
N_2	...	....	....	0.04
Total	2.040	1.09	1.90	0.04

$$\text{Dry air theoretically required} = \frac{2.04}{0.21} = 9.72 \text{ cu. m. (1).}$$

$$\text{Excess air, dry} = 0.20 \times 9.72 = \underline{1.94}$$

$$\text{Total dry air} = 11.66 \text{ cu. m}$$

Since the moist air is 1.5 per cent H_2O, it is 98.5 per cent dry air; therefore, the 11.66 cu. m. of dry air constitutes 98.5 per cent of the moist air.

$$\text{Then total moist air} = \frac{11.66}{0.985} = 11.84 \text{ cu. m. (2).}$$

$$H_2O \text{ in moist air} = 11.84 - 11.66 = 0.18 \text{ cu. m.}$$

$$O_2 \text{ in excess air} = 0.21 \times 1.94 = 0.41$$

$$N_2 \text{ in total air} = 0.79 \times 11.66 = 9.21$$

$$\text{Total } N_2 \text{ in products of combustion} = 9.21 + 0.04 = 9.25 \text{ cu. m.}$$

$$\text{Total } H_2O \text{ in products of combustion} = 1.90 + 0.18 = 2.08$$

$$CO_2 = 1.09$$

$$O_2 = \underline{0.41}$$

$$\text{Total products of combustion} = 12.83 \text{ cu. m. (3).}$$

Summary.—The various items that may be included in the "products of combustion" may be listed as follows:

1. Gases formed according to the equations.
2. Gases liberated directly from the fuel.
3. Nitrogen from the air.
4. Oxygen from the excess air.
5. Moisture from the air.

The following example will illustrate collectively the principles so far given in this chapter:

Example 3 ✓

Big Eagle coal from West Virginia has the composition:

	Per Cent		Per Cent
C	79.1	S	0.9
H	6.9	H_2O	1.8
O	6.6	Ash	3.3
N	1.4		

The flue gases from a furnace using this coal were analyzed and found to contain 6.4 per cent free oxygen, dry analysis.

The ashes from the furnace contained 20 per cent unburned carbon.

The atmospheric conditions were: temperature, 61°F.; barometer, 30.3 in.; humidity, 58 per cent.

Required: 1. The cubic meters of dry air at standard conditions theoretically required, per kilogram of coal.

2. The percentage of excess air used.

3. The cubic meters of moist air actually used per kilogram of coal, measured at the given conditions.

4. The percentage composition of the flue gases, wet.

Solution:

Ashes = ash + unburned carbon.

The unburned carbon being 20 per cent of the ashes, the other 80 per cent is "ash," which from the analysis would be 0.033 kg. in 1 kg. of coal. The ashes, therefore, weigh $\frac{0.033}{0.80} = 0.041$ kg, and the carbon unburned is $0.041 - 0.033 = 0.008$ kg.

The weight of carbon burned per kilogram of coal is then $0.791 - 0.008 = 0.783$ kg.

$$C + O_2 = CO_2 \quad \ldots \quad O_2 = 0.783 \times \frac{22.4}{12} = 1.462 \text{ cu. m.}$$

$$2H_2 + O_2 = 2H_2O \quad \ldots \quad O_2 = 0.069 \times \frac{22.4}{4} = 0.386$$

$$S + O_2 = SO_2 \quad \ldots\ldots\ldots\ldots \quad O_2 = 0.009 \times \frac{22.4}{32} = 0.006$$

$$\text{Total } O_2 \text{ required} = \overline{1.854} \text{ cu. m.}$$

$$O_2 \text{ present in coal} = 0.066 \times \frac{22.4}{32} = 0.046$$

$$O_2 \text{ required from air} = \overline{1.808} \text{ cu. m.}$$

Air theoretically required $= \frac{1.808}{0.21} = 8.61$ cu. m. per kilogram of coal (1).

Free oxygen amounting to 6.4 per cent of the dry flue gases represents excess air, which would amount to $\frac{6.4}{0.21} = 30.5$ per cent of the flue gases. The flue gases exclusive of excess air are 100 − 30.5, or 69.5 per cent of the entire flue gases (dry). To find the dry flue gases exclusive of excess air:

CO_2 formed = same as O_2 for C = 1.462 cu. m.
H_2O formed (omit from *dry* flue gases)
SO_2 formed = same as O_2 for S = 0.006
N_2 in coal $= 0.014 \times \frac{22.4}{28} = 0.011$
N_2 from air $= 8.61 - 1.808 = 6.802$
Total dry flue gases = 8.281 cu. m.

Dry flue gases including excess air $= \frac{8.281}{0.695} = 11.92$ cu. m.

Excess air = 11.92 − 8.28 = 3.64 cu. m.

Percentage of excess air used $= \frac{3.64}{8.61} = 42.3$ per cent (2).

Total dry air used = 8.61 + 3.64 = 12.25 cu. m. at standard conditions.
Temperature = 61°F. = $(61 - 32)\frac{5}{9}$ = 16°C.
From Table XXIV (p. 401), maximum pressure of water at 16°C. = 13.6 mm.
Humidity 58 per cent; therefore, actual pressure = 0.58 × 13.6 = 7.9 mm.
Barometer = 30.3 in. × 25.4 = 770 mm.

Moist air at given conditions $= 12.25 \times \frac{273 + 16}{273} \times \frac{760}{770 - 7.9} = 12.93$ cu. m. (3).

H_2O formed from H_2 = twice O_2 for H_2 = 0.772 cu. m.
H_2O in coal $= 0.018 \times \frac{22.4}{18} = 0.022$
H_2O in air $= \frac{7.9}{770 - 7.9} \times 12.25 = 0.127$
Total H_2O = 0.921 cu. m.
O_2 in excess air = 0.21 × 3.64 = 0.764
Total N_2 = (0.79 × 12.25) + 0.011 = 9.688 cu. m.

Percentage composition:

Gas	Cubic meters	Per cent
CO_2	1.462	11.39
H_2O	0.921	7.17
SO_2	0.006	0.05
O_2	0.764	5.94
N_2	9.688	75.45
Total	12.841	100.00

Calorific Power.—The quantity of heat generated by completely burning one unit of a fuel is known as the *calorific power* or *heating value* of the fuel. For solid or liquid fuels it is usually expressed in calories per gram (= Calories per kilogram) or in B.t.u. per pound. For gases it is usually expressed in calories per liter (= Calories per cubic meter) or in B.t.u. per cubic foot.

The calorific power may be determined directly by burning a small weighed portion of the fuel in a calorimeter and measuring the heat liberated. When the percentage composition of the fuel is known, the calorific power may be computed approximately from the analysis by adding together the heating values of the different combustible elements in it, each multiplied by the percentage present, and applying certain corrections as described below. The calorific power depends directly on the chemical composition and not on the conditions under which the fuel is burned, since the definition of calorific power assumes complete combustion. It is thus an important specification for the buyer and seller of fuel. As such it cannot vary with the conditions under which the fuel is to be used, and the seller is not cognizant of what these conditions will be.

The *actual* amount of heat obtained from a fuel *as burned* is usually a little less than the calorific power, because of imperfect or incomplete combustion. The actual amount of heat obtained may be calculated when the conditions pertaining to the combustion are fully known.

Calculation of heating value of fuels from the analysis is very useful in practice; the values so obtained are found to check closely—for most fuels within 1 or 2 per cent—with the values determined by calorimeter. Let it be required to figure the calorific power of 1 kg. of the coal given in Example 3. The analysis was: C, 79.1 per cent; H, 6.9; O, 6.6; N, 1.4; S, 0.9; H_2O, 1.8; ash, 3.3. The combustible or heat-giving constituents are the carbon, hydrogen, and sulphur. The heat produced by 1 kg. of carbon is usually taken as 8,100 Cal. This value is somewhat uncertain, since it varies for different forms of carbon. The best determination of the calorific power of pure crystalline carbon, in the form of diamond, puts it at 7,870 Cal. per kilogram. But for amorphous carbon, as it exists in fuels, the value is considerably higher. Determinations with amorphous carbon in various forms have fallen mostly between 8,050 and 8,150, and there seems to be no reason to depart from the value of 8,100, which has long been in use, though some engineers now prefer the value 8,080. Apparently 8,100 can be adopted with a probable error of less than ± 1 per cent. The carbon in the above coal then yields $0.791 \times 8,100 = 6,407$ Cal.

Determinations of the calorific power of hydrogen have fixed this value at 33,920 Cal. per kilogram. In view of the uncertainty in the figure for carbon, it is permissible to round off the figure for hydrogen to 34,000, which will accordingly be used in this book for calculating calorific powers. Not all the hydrogen in coal, however, will supply heat when the coal is burned, since some of it is already chemically combined with the oxygen contained in the coal. The amount estimated to be combined with the oxygen must be deducted from the total hydrogen before multiplying by 34,000. The amount so combined is evidently uncertain, but it is customary to assume that the oxygen in the coal is combined with hydrogen in the same proportion as in water. Water is 2 parts hydrogen to 16 parts oxygen by weight. Therefore, from the hydrogen shown in the analysis, there is deducted an amount of hydrogen equal to one-eighth the oxygen. Hydrogen in the above coal then yields $\left(0.069 - \frac{0.066}{8}\right) 34{,}000 = 2{,}066$ Cal.

The calorific power of sulphur is 2,212 Cal. per kilogram; and since the amount of sulphur in fuel is always small, this figure may be rounded to 2,200. Heat contributed by sulphur in the above coal is then $0.009 \times 2{,}200 = 20$ Cal.

The calorific power of the coal is the sum of $6{,}407 + 2{,}066 + 20 = 8{,}493$ Cal., when the assumption is made that all the H_2O vapor formed is condensed to water. This is designated the *high, gross,* or *calorimetric* calorific power.

In furnace practice the products of combustion leave the furnace at high temperature so that the water vapor cannot condense as it does in a calorimeter. When water vapor condenses, it liberates its latent heat of vaporization, and this is included in the figures above. In practical combustion, however, this heat will not become available; consequently a deduction should be made from the above, not only for the H_2O formed from the hydrogen, but also for the H_2O present as moisture in the coal, here shown in the analysis as 1.8 per cent. Burning the coal causes its moisture content to evaporate and so absorb heat. The latent heat of vaporization of H_2O is 539 Cal. per kilogram when the water is at the boiling point. Here, however, the water may be assumed to be at room temperature, and additional heat is therefore required to evaporate it. Regnault's value of 606.5 Cal. per kilogram is often used for the total heat absorption. But since steam tables give 586 Cal. per kilogram as the quantity of heat to vaporize water at 18°C., and this figure corresponds exactly to the difference between the heat liberated in forming liquid water and the heat liberated in forming water vapor from hydrogen and oxygen at 18°C., as given in tables of heats of formation, the figure 586 will here be adopted.

In burning the above coal the total amount of water vapor will be $(1\frac{8}{2} \times 0.069) + 0.018 = 0.639$ kg., and the latent heat will then be $0.639 \times 586 = 374$ Cal. The corrected calorific power then is $8{,}493 - 374 = 8{,}119$ Cal.

The calorific power corrected as above for heat absorbed in vaporization of water is called the *low, net,* or *practical* calorific power. It evidently is of greater significance to the engineer than the high calorific power, and in this book the term "calorific power" will be assumed to refer to this lower value unless otherwise stated.

The precise value to be used for the heat of vaporization differs for different cases and for different purposes. Strictly, it would not be the same for the water vapor formed by combustion of hydrogen as for the vaporization of liquid moisture. In the former case the true correction is the difference between the heat of combustion of hydrogen as measured by the calorimeter and the heat of combustion as it takes place in the furnace. In the calorimeter most of the water vapor resulting from the combustion condenses and gives up the heat of vaporization. In a constant-volume calorimeter, such as the bomb type, the condensation is practically complete, but in a constant-pressure calorimeter of the Junkers gas type 10 to 20 per cent of the vapor may escape uncondensed. More important to note, however, is the fact that the vapor does not condense at 100°C. None can condense until the "dew point" of the mixture is reached, and this will usually be in the neighborhood of 60°C. Even there condensation only *begins;* and since the vapor is cooling rapidly, the greater part of it will not condense until about room temperature. If it is assumed to condense at 18°, the heat given up is 586 Cal. per kilogram. No heat should be added to this for the cooling of the vapor from 100° down to 18°, any more than we add anything to the 8,100 Cal. for carbon for the cooling of CO_2.

In calculating furnace efficiencies and heat balances, the furnace would be charged with the low calorific power of the fuel. Among the heat losses would be included the heat carried out in the hot flue gases. In computing this quantity, only the sensible heat content will be included; the heat of vaporization of the H_2O will not be included because it has been deducted in obtaining the low calorific power. The sensible heat content of all the gases will usually be figured from the actual temperature down to 0°. This places the H_2O on the same basis as all the other gases and prevents confusion. The only inaccuracy introduced is that the heat is figured to 0° instead of to 18°, but this is a negligible error and applies to the other gases just as to the H_2O.

In the latter case, above—the heat absorbed by vaporization of the liquid moisture content of the fuel—the problem is different. Here the liquid begins to vaporize as soon as the fuel begins to heat up; but normally the fuel will heat so quickly that very little will have vaporized until the temperature is 100°C. or higher. At this temperature (100°), the heat of vaporization is 539 Cal. But the H_2O has been heated *as liquid* to 100°, which requires (from 18° to 100°) an additional 82 Cal., making 621 Cal. total absorbed. But since the heat carried out in the H_2O vapor will include the sensible heat in the vapor all the way down to 0°, there should be deducted from 621 the heat content of H_2O vapor at 100°, which is 47 Cal. This leaves 574 Cal. However, the difference between 574 and 586 is small, and the amount of moisture contained in fuel is likewise usually small, so that no appreciable error is made in using 586 for the entire amount of H_2O. In correcting calorimetrically measured high calorific powers to obtain the low calorific powers, it is possible that a different value might be preferable, perhaps nearer Regnault's figure of 606.5.

Dulong's Formula.—Dulong summarized the calculation of calorific power from analysis in a formula, which may be stated as follows, using constants to agree with the values used above:

$$\text{Low calorific power} = 8{,}100\ C + 34{,}000\left(H - \frac{O}{8}\right) + 2{,}200\ S - 586\ (9\ H + W).$$

The symbols represent fractions of a kilogram of the various constituents as shown in the analysis.

The corresponding formula in B.t.u. per pound is:

$$\text{Low calorific power} = 14{,}600\ C + 61{,}000\left(H - \frac{O}{8}\right) + 4{,}000\ S - 1{,}050\ (9\ H + W)$$

Calorific Power of Liquid Fuels.—Because of the relatively large amount of hydrogen contained in crude oil and other fuels of the hydrocarbon type and the complexity of the chemical combinations of carbon, hydrogen, and oxygen in these fuels, the probable error in applying Dulong's formula to calculate the calorific power is greater than in the case of coal and similar fuels. The error may be as high as 8 per cent. Nevertheless, Dulong's formula is often used when only an approximate value is needed.

The calorific powers of fuel oils of this type are found to vary proportionately with their specific gravities, the lighter oils having the higher calorific powers. An approximate empirical formula for calculation of the high calorific powers of fuel oils from their gravities expressed in degrees Baumé is as follows:[1]

$$\text{B.t.u. per pound} = 18{,}650 + 40\,(\text{degrees Baumé} - 10).$$

The calorific power (high) of fuel oils is usually between 10,000 and 11,000 Cal. per kilogram, or 18,000 and 19,500 B.t.u. per pound.

Calorific Power of Gases.—The calorific power of a gaseous fuel may likewise be determined from the sum of the calorific powers of the constituent gases. In this case any H_2O contained is already in the vapor state. There is no latent heat to be corrected for, if the lower heating values of the constituent gases are used. The calorimeter would, of course, measure the higher calorific power of a gas, and a determination so made is ordinarily corrected in accordance with the principles given above. The lower calorific powers of the principal fuel gases are given for convenient reference in Table II. A more extended table of calorific powers of gases and liquids is given on page 422.

TABLE II.—CALORIFIC POWERS (LOW) OF COMMON FUEL GASES

Gas	Calories per cubic meter[1]	B.t.u. per cubic foot[1]
CO	3,034	341
H_2	2,582	290
CH_4	8,560	962
C_2H_2	13,440	1,510
C_2H_4	14,480	1,627
C_6H_6	33,490	3,763

[1] At standard conditions, 0°C., 760 mm., or 32°F., 29.92 in.

Heat Losses in Combustion.—If a furnace process were thermally 100 per cent efficient, all the heat available as calorific power in the fuel would be utilized in the process. Obviously, however, only a small portion of it is so utilized, and the balance is lost in various ways. The losses may be classified as follows:

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[1] SHERMAN, H. C., and A. H. KROPFF, *J. Am. Chem. Soc.*, **30**, 1626 (1908).

1. Unburned fuel in the ashes.
2. Carbon burned to CO instead of CO_2.
3. Heat carried out of the furnace in the hot flue gases
4. Heat carried out in other waste products and in cooling water.
5. Heat transferred to the ground, the furnace, and surroundings by conduction, convection, and radiation.

The calculation of the amount of item 1 is obvious when the amount of unburned carbon in the ashes has been determined.

When carbon burns to CO, it enters a lower state of oxidation than when it burns to CO_2, and a smaller amount of heat is generated. Oxidation of 1 kg. of carbon to CO produces 2,430 Cal., as against 8,100 Cal. when oxidized to CO_2. Analysis of the flue gases and determination of the percentage of CO in them make item 2 readily determined.

Calculation of item 3 requires knowing the temperature of the flue gases leaving the furnace and a knowledge of the principles involved in calculating the heat content of a hot body. This will now be considered; calculation of items 4 and 5 will be taken up later in the book.

Heat Energy and "Heat Content."—Heat is a transient form of energy. Heat (q) entering a body at constant pressure becomes part of "heat content" (H) of the body,[1] while heat flow from a body *decreases* the heat content thereof. Accordingly we may write:

$$q = -\Delta H.$$

Although heat is translated into other forms of energy on entering a body, the metallurgist is so much concerned with the heat requirements of furnaces, processes, etc., that it is customary for convenience to consider heat as though it remained an entity and to speak of the "heat content" of bodies. Again for convenience, we shall calculate heat content with 0°C. as a base line, obtaining not the total heat content but the content above 0°C. The expressions used for specific heats of substances will be given in the form of the specific heat at 0°C. plus a term or terms for the change in specific heat per degree centigrade.

Calculation of Developed Heat Content (Sensible Heat).—When it was stated that complete combustion of 1 kg. of carbon liberates 8,100 Cal., it was understood that the figure corresponded to an experimental determination made in a calorimeter, the carbon being at room temperature (*i.e.*, approximately at 18°C.) when burned. If 1 kg. of glowing hot carbon is burned, a considerably greater amount of heat is obtained; it is found that the total is the sum of two components, (1) a latent quantity of heat equal to the calorific power (8,100 Cal.), plus (2) a developed, or

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[1] In thermodynamics, heat content is usually called *enthalpy*.

"sensible," quantity of heat equal to the amount of heat required to make the carbon incandescent, *i.e.*, to raise it from room temperature to the temperature it actually possessed when burned. (Both the above cases presuppose that the oxygen used to burn the carbon was at room temperature. If it were hot, a still greater amount of heat would be available. The heat available due to the carbon itself would be the same, but the total would be increased by the heat content of the oxygen.) As regards the energy content of the hot carbon, evidently it is divisible into two categories, as follows: undeveloped, or chemically latent, energy, which will be developed as heat when the carbon burns, and developed, or sensible, heat, which made the carbon hot before it burned.

The Calorie is equal (approximately) to the quantity of heat required to raise the temperature of 1 kg. of water 1°C. To raise the temperature of 1 kg. of carbon 1°C. requires 0.206 Cal. (at 0°C.), which is called the *specific heat* of carbon. Evidently to raise the temperature of the carbon to 10°C. would require 2.06 Cal., and this would be the heat content of 1 kg. of carbon at 10°C. (measured from 0°C.). The general relation is:

Sensible heat content per kilogram = specific heat × temperature

and

Total sensible heat content = quantity × specific heat × temperature.

The specific heat of substances, however, increases as the temperature rises, so that in applying the relation just stated it would not be correct to use the specific heat at 0°C. or at the actual temperature; the mean specific heat between these two points must be used. If Q be the heat content in Calories at temperature t°C., W the weight in kilograms, c_m the mean specific heat per kilogram between 0 and $t°$, the relation becomes:

$$Q = Wc_mt.$$

The corresponding volumetric relation for gases would be $Q = Vc_mt$, where c_m is the mean specific heat per cubic meter if V is expressed in cubic meters. Specific heat is discussed further in Chap. V.

The change of specific heat with temperature can best be expressed in the form $A + Bt + Ct^2$, or $A + Bt - Ct^{-2}$, where A is the specific heat at 0°C. and B and C are constants determinable by experiment for various substances.[1] For most purposes it is sufficiently accurate to use an expression of the form $A + Bt$, although this form does not fully represent the shape of the curve giving the variation.

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[1] For expression of heat content in the form of an integral and calculation by integration, see p. 88.

When this form is used, if the specific heat at $t°$ is $A + Bt$, the mean specific heat between 0 and $t°$ is $A + \frac{1}{2}Bt$. In the reference tables it will be more useful to give the expressions for mean specific heats between 0 and $t°$ than for the actual specific heats at $t°$.

If it be desired to find the change in heat content of a body whose temperature changes from t_1 to t_2, we should proceed as follows:

Heat content at $t_1 = W(A + Bt_1)t_1 = WAt_1 + WBt_1^2$.
Heat content at $t_2 = W(A + Bt_2)t_2 = WAt_2 + WBt_2^2$.

Subtracting:

Change in heat content $= WA(t_1 - t_2) + WB(t_1^2 - t_2^2) = W[A + B(t_1 + t_2)](t_1 - t_2)$.

It is here noted that the temperature change is the multiplying factor outside the bracket, but inside the bracket the factor is the *sum* of the two temperatures.

As an example, let it be required to calculate the heat content of the flue gases of Example 3, assuming their temperature to be 1000°C. The constituent gases and their volumes were CO_2, 1.462 cu. m.; H_2O, 0.921; SO_2, 0.006; O_2, 0.764; N_2, 9.688. The mean specific heats of these gases per cubic meter (measured at standard conditions) between 0 and $t°$ are as follows:[1]

CO_2 and SO_2: $0.406 + 0.000090t$.
H_2O: $0.373 + 0.000050t$.
O_2 and N_2: $0.302 + 0.000022t$.

The heat contents (above 0°C.) are, therefore:

In CO_2 and SO_2: $1.468(0.406 + 0.00009 \times 1{,}000)1{,}000 =$ 728 Cal.
In H_2O: $0.921(0.373 + 0.00005 \times 1{,}000)1{,}000 =$ 390
In O_2 and N_2: $10.452(0.302 + 0.000022 \times 1{,}000)1{,}000 =$ 3,386
Total = 4,504 Cal.

As the calorific power of the coal was computed to be 8,119 Cal., $\frac{4{,}504}{8{,}119}$, or 55 per cent, of the heating value of the coal would be carried out by the flue gases at 1000°C.

Temperature Attained in Combustion.—When a fuel is burned, it disappears as such, together with the oxygen used in burning it, and there results a mixture of gases which take up the heat generated from the calorific power of the fuel and any sensible heat present in the fuel or the air before combustion took place. This heat is sufficient in quantity to heat the gaseous products to a high temperature, giving rise to the phenomenon known as *flame*. The flame temperature is the maximum temperature attained by the combustion. It is sometimes called the *calorific intensity*.

If the assumption is made that all the heat available or generated in combustion is present in the gases immediately after combustion, then this quantity of heat is equal to the sensible heat in the gases at their temperature t and an equation results from which the value of t can be calculated. The assumption obviously is not wholly true, since some heat will be lost to the surroundings while combustion is taking place. Not all of it will be taken up by the gaseous products of combustion even momentarily, and consequently the actual maximum temperature attained will be somewhat less than the theoretically calculated maximum. An additional source of error results from the uncertainty regarding the accuracy of the values for specific heats of gases at high temperatures, which error may either increase or counteract the other. Nevertheless, the calculated result is sufficiently close to be very useful for comparative purposes, and the principles involved in the calculation are very instructive as regards the nature of combustion and the relation between quantity of heat supplied and temperature resulting.

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[1] Derived from constants given by E. D. Eastman, "Specific Heats of Gases at High Temperatures," *U. S. Bur. Mines, Tech. Paper* 445, 1929.

We have:

$$\text{Total heat available} = \text{heat in products of combustion},$$

or,

$$\text{Calorific power} + \text{sensible heat in fuel} + \text{sensible heat in air} = \text{volume of gases} \times \text{specific heat} \times \text{temperature}$$

whence,

$$\text{Temperature} = \frac{\text{calories available}}{\text{volume of gases} \times \text{specific heat}}.$$

Example 4

Calculate the flame temperature of the natural gas in Example 2 (p. 22):

1. Burned with the theoretical requirement of dry air, with sensible heat in both the natural gas and the air negligible.
2. Burned with 20 per cent excess air, moist, as specified in Example 2, and with the air preheated to 600°C. before combustion.

Solution: The products of combustion under theoretical conditions consist of (see p. 22):

$$CO_2 = 1.09 \text{ cu. m.}$$
$$H_2O = 1.90$$
$$N_2 = (9.72 - 2.04) + 0.04 = 7.72$$

The calorific power of the gas is:

From CH_4: $0.85 \times 8,560 = 7,276$ Cal.
From C_2H_4: $0.03 \times 14,480 = 434$
From C_6H_6: $0.03 \times 33,490 = 1,005$
From H_2: $0.05 \times 2,582 = 129$
Total = 8,844 Cal. per cubic meter

Then:

$$\begin{aligned} 8,844 = {} & 1.09(0.406 + 0.00009t)t \\ & + 1.90(0.373 + 0.00005t)t \\ & + 7.72(0.302 + 0.000022t)t \end{aligned}$$

or

$$8,844 = 3.483t + 0.000363t^2.$$

Solving the equation:

$$t = 2090°\text{C. (1).}$$

With 20 per cent excess air, moist, there was used 11.66 cu. m. of dry air and 0.18 cu. m. of H_2O. This is preheated to 600°.

$$\begin{aligned} 11.66(0.302 + 0.000022 \times 600)600 &= 2{,}205 \text{ Cal.} \\ 0.18(0.373 + 0.00005 \times 600)600 &= \underline{\phantom{0{,}0}43} \\ \text{Total sensible heat in moist air} &= 2{,}248 \text{ Cal.} \\ \text{Calorific power} &= \underline{8{,}844} \\ \text{Total heat available} &= 11{,}092 \text{ Cal.} \end{aligned}$$

The products of combustion are now increased by the excess air and the moisture of the air. Their totals as found in Example 2 are CO_2, 1.09; H_2O, 2.08; N_2 and O_2, 9.66.

Then:

$$\begin{aligned} 11{,}092 = {} & 1.09(0.406 + 0.00009t)t \\ & + 2.08(0.373 + 0.00005t)t \\ & + 9.66(0.302 + 0.000022t)t \end{aligned}$$

or

$$11{,}092 = 4.136t + 0.000415t^2.$$

Solving:

$$t = 2200°\text{C. (2).}$$

Regenerative Furnaces and Waste-heat Boilers.—When the flue gases leave a furnace at very high temperature, as in an open-hearth steel furnace or a reverberatory copper-smelting furnace, the heat contained in them would entail a huge loss were not means taken to recover a large part of it. One means of recovery is by allowing the hot flue gases to pass through a brick checkerwork immediately after leaving the furnace proper, causing the brick to heat up and thereby absorb a great deal of heat from the gases, which leave the "checkers" several hundred degrees cooler than when they entered. The incoming air used for combustion in the furnace, and the fuel gas also if the furnace is fired with producer gas or a similar gas, then passes through the hot checkers, the flow having been changed by a reversing valve, and becomes heated by absorbing the heat from the checkers. Thus this heat is carried back into the furnace again, not only saving it, but also increasing the temperature in the furnace by preheating in accordance with the principles illustrated in Example 4. This manner of saving heat and raising the furnace temperature is termed *regeneration*.

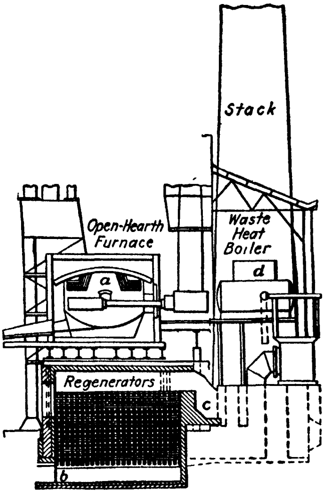

FIG. 1.—Diagram illustrating flow of gaseous products of combustion in lay-out of open-hearth plant: *a*, gases in furnace; *b*, entering regenerators; *c*, leaving regenerators to enter waste-heat boiler; *d*, entering stack. (Spacing of units has been modified to simplify illustration.)

Another method of saving heat is to cause the flue gases to pass through a "waste-heat boiler," which produces steam in the same manner as an ordinary boiler. Often a furnace is provided with both means of heat economy, the hot gases going first through the checkers and then through a waste-heat boiler (see Fig. 1).

Knowing the composition of the flue gases and the temperature at the various points in such a system, one may readily calculate the heat content of the gases at the different points and by subtraction find the heat given up in the furnace proper, the checkers, the waste-heat boiler, etc. The thermal efficiency of the checkers may then be determined if it is known to what temperature they preheat the incoming air or gas, and the efficiency of the boiler may be calculated from the steam data. A simplified example will suffice as an illustration.

Example 5

The natural gas of Example 2 is used in a regenerative furnace, using 20 per cent excess air, the air being moist as in Example 2. The flue gases leave the furnace at 1500°C. and enter regenerators at that temperature. They leave the regenerators at 800°C., passing directly to a waste-heat boiler. They leave the boiler at 350°C.

The regenerators preheat the incoming air to 600°C. The boiler develops 0.2 boiler hp. for each cubic meter of natural gas burned per hour.

Required: 1. The heat given up by the flue gases, per cubic meter of natural gas burned:

a. In the furnace proper.
b. In the regenerators.
c. In the boiler.

2. The thermal efficiency of the regenerators and of the boiler.

Solution: The products of combustion have been found (p. 22). They are: CO_2, 1.09 cu. m.; H_2O, 2.08; O_2 and N_2, 9.66. The heat capacity of these gases at any temperature t is:

$$\begin{aligned}
CO_2\text{: } 1.09(0.406 + 0.00009t)t &= 0.443t + 0.000099t^2 \\
H_2O\text{: } 2.08(0.373 + 0.00005t)t &= 0.776t + 0.000104t^2 \\
N_2 \text{ and } O_2\text{: } 9.66(0.302 + 0.000022t)t &= \underline{2.917t + 0.000212t^2} \\
\text{Total} &= 4.136t + 0.000415t^2
\end{aligned}$$

When

t = 1500°, the gases contain $4.136 \times 1{,}500 + 0.000415 \times 1{,}500^2 = 7{,}138$ Cal.
t = 800°, the gases contain 3,574
t = 350°, the gases contain 1,498

The total heat entering the furnace (found on p. 33) was 11,092 Cal.

Heat given up in furnace proper = 11,092 − 7,138 = 3,954 Cal. (*a*).
Heat given up in regenerators = 7,138 − 3,574 = 3,564 Cal. (*b*).
Heat given up in boiler = 3,574 − 1,498 = 2,076 Cal. (*c*).

The heat imparted to the air preheated to 600°C. (found on p. 33) was 2,248 Cal. The heat entering the regenerators was 7,138 Cal. Thermal efficiency $= \frac{2{,}248}{7{,}138} = 31$ per cent (2*a*).

By definition, 1 boiler hp. evaporates 34.5 lb. of water per hour from and at 212°F. To evaporate 1 lb. of water requires 971 B.t.u., or 244.4 Cal. Therefore, 1 boiler hp. is equivalent to 244.4 × 34.5 = 8,440 Cal. per hour.

0.2 boiler hp. per cubic meter × 8,440 = 1,688 Cal. utilized in boiler per cubic meter of gas burned.

The heat entering the boiler was 3,574 Cal.; $\frac{1,688}{3,574} = 47$ per cent (2*b*).

Problems

NOTE: The problems on combustion assume perfect combustion of the fuel in the sense that all the carbon burned goes to CO_2 and all the hydrogen to H_2O. The term "theoretical" air designates the amount as determined by the equations, without excess air; it does not mean that all the carbon in the fuel is assumed to burn. Even in calculating the theoretical air requirement, the amount of carbon left unburned in the ashes is to be deducted from the total carbon in the fuel before computing the oxygen requirement from the equations. In certain cases, combustion may be imperfect, *i.e*, some of the carbon may burn to CO instead of CO_2; when this is the case, the statement of the problem will definitely make this point clear.

10. A furnace used for melting brass uses coke as a fuel. The composition of the coke is as follows:

	Per Cent
C	82
H	4
H_2O	2
Ash	12

The ashes from the furnace amount to 15 per cent of the weight of the coke. 60 per cent more air is used than theoretically required.

Required: 1. The cubic meters of air theoretically required for combustion of 1 kg. of the coke. Calculate by the weight method.

2. The volume of air actually used per kilogram of coke. Calculate by the volume method.

3. The volume of the products of combustion (flue gases) when using only the theoretical requirement of air. Calculate by weight and change to volume.

4. The volume and percentage composition of the products of combustion as actually formed (*i.e.*, including excess air) Calculate directly by the volume method

11. A smelting furnace burns powdered coal of the following composition:

	Per Cent		Per Cent
C	76.0	S	1.2
H	4 9	H_2O	1.5
O	7.8	Ash	6.9
N	1.7		

The burners are supplied with 30 per cent more air than theoretically required for complete combustion.

Required: 1. Per kilogram of coal, the kilograms of air supplied.

2. Per kilogram of coal, the cubic meters of air supplied. Calculate both from the result of requirement 1 and also by the direct volume method.

3. Per pound of coal, the cubic feet of air supplied.

4. Per kilogram of coal, the total weight of the products of combustion.

5. Per kilogram of coal, the total cubic meters of products of combustion. Use the direct volume method.

6. Per pound of coal, the cubic feet of products of combustion.

12. A sample of charcoal has the following analysis:

	Per Cent
C	87.43
H	2.26
O	0.54
H_2O	8.21
Ash	1.56

The charcoal is burned with 20 per cent more air than is theoretically required The air is at 15°C. and barometric pressure of 748 mm., assumed dry. The ashes amount to 2 per cent of the weight of the charcoal.

Required: 1. The volume of air, in cubic feet at standard conditions, theoretically required to burn 1 lb. of charcoal, calculated by the weight method.

2. The same, calculated by the direct volume method.

3. The volume of air actually used, at the conditions given.

4. The weight of air used, in pounds.

5. The volume and percentage composition of the products of combustion.

6. The weight of the products of combustion.

13. A metallurgical furnace uses bituminous coal of the following composition:

	Per Cent		Per Cent
C	72.2	O	7.8
H	5.0	S	0.8
N	1.7	Ash	12.5

The ashes from the furnace are one-fourth unburned carbon. The outside air is at 22°C. and 751 mm. barometric pressure. 50 per cent more air is used than the theoretical requirement.

Required: 1. The cubic feet of air (at standard conditions) theoretically required to burn 1 lb. of coal

2. The cubic feet of air actually used at the given conditions

3. The volume of the products of combustion (flue gases) in cubic feet, and their percentage composition.

4. The cubic meters of air (at standard conditions) actually used, per kilogram of coal.

5. The volume of the products of combustion in cubic meters, and their percentage composition.

14. A furnace burns in 24 hr. 9½ metric tons of the following coal:

	Per Cent
C	76.0
H	4.5
O	12.5
H_2O	1.0
Ash	6.0

980 kg. of ashes is made. The total volume of flue gases leaving the stack in 24 hr. is 228,000 cu. m., measured at the stack temperature of 330°C, and pressure of 725 mm.

Required: 1. The cubic meters of air theoretically required to burn the coal, at standard conditions.

2. The percentage excess air used.

15. A sample of coal has the following composition:

	Per Cent		Per Cent
C	73.9	N	1.4
H	4.8	H_2O	5.4
O	8.8	Ash	5.7

When the coal was used in a furnace, the ashes contained 18 per cent carbon and the flue gases analyzed 12 per cent free oxygen, dry analysis.

Required: 1. The theoretical requirement of air, in cubic feet per pound of coal

2. The volume of air actually used, and the percentage excess air.

3. The percentage composition of the total flue gases, wet analysis.

16. A coal has the following analysis:

	Per Cent		Per Cent
C	53.76	N	0.76
H	4.44	H_2O	2.73
O	12.54	Ash	21.76
S	4.01		

It is burned in a furnace, using 40 per cent excess air. The ashes from the furnace are 25 per cent unburned carbon.

The air temperature is 18°C. and barometric pressure 740 mm.; air assumed dry.

Required: 1. The volume of air theoretically required to burn 1 kg. of coal, at standard conditions.

2. The volume actually used, under the conditions given.

3. The percentage composition of the products of combustion.

4. The grams of moisture carried by each cubic meter of the products of combustion.

17. An open-hearth steel furnace is fired with producer gas that analyzes as follows:

	Per Cent		Per Cent
CO	24.4	CH_4	4.0
CO_2	4.9	N_2	53.7
H_2	10.2	H_2O	2.8

In burning it, 10 per cent excess air is used. The air and gas enter the ports of the furnace at a temperature of 500°C., pressure 800 mm. The products of combustion leave the furnace at 1500°C., 750 mm.

Required: 1. Per cubic meter of gas at standard conditions, the cubic meters of air used at standard conditions.

2. Per cubic foot of gas at the given conditions, the cubic feet of air used at the given conditions.

3. Per cubic foot of gas at the given conditions, the cubic feet of air measured at standard conditions.

4. Per cubic meter of gas at standard conditions, the cubic meters of the products of combustion at standard conditions, and their percentage composition.

5. Per cubic meter of gas at standard conditions, the cubic meters of total products of combustion measured at the conditions under which they leave the furnace.

6. Per cubic foot of gas under the given conditions, the total cubic meters of products of combustion as they leave the furnace.

18. A zinc plant uses natural gas as fuel. The gas issues from the pipes at 20°C., 940 mm. The outside air is at 10 below 0°C., 720 mm., and the air is preheated to 500°C. before using.

The composition of the gas is as follows:

	Per Cent		Per Cent
CH_4	94.2	CO	0.8
C_2H_4	0.8	CO_2	0.4
O_2	0.6	N_2	3.2

Required: 1. The cubic feet of air used to burn 1 cu. ft. of gas, allowing 10 per cent excess and measuring the gas at the conditions as obtained from the pipes, and the air at the outside conditions.

2. The same, but with the air measured as preheated.

3. The products of combustion at standard conditions, per cubic foot of gas at standard conditions.

4. The products of combustion at standard conditions per cubic foot of gas under the conditions as obtained.

19. The composition of a fuel gas is as follows:

	Per Cent		Per Cent
H_2	40	CO	18
CH_4	22	O_2	1
C_2H_4	7	CO_2	3
N_2	4	H_2O	5

In burning it, air is supplied to an amount 15 per cent in excess of the theoretical requirement.

Required: 1. The cubic meters of air used to burn 1 cu. m. of gas.

2. The cubic meters of the products of combustion from 1 cu. m. of gas, and their percentage composition.

3. The weight in kilograms of 1 cu. m. of gas and of 1 cu. m. of the products of combustion.

4. The weight of air used to burn 1 kg. of gas.

5. The grams of water vapor contained in 1 cu. m. of the gas and in 1 cu. m. of the products of combustion.

20. Natural gas analyzed as follows:

	Per Cent
CH_4	82
H_2	4
CO	5
CO_2	7
N_2	2

The gas flows from the pipe at a temperature of −8°C., pressure 820 mm., and is burned with air that has a temperature of 30°C., pressure 735 mm. The products of combustion carry 3 per cent free oxygen.

Required: 1. The cubic meters of air used to burn 1 cu. m. of gas, both measured at standard conditions, and the percentage excess air used.

2. The percentage composition of the products of combustion.

3. The cubic meters of air used to burn 1 cu. m. of gas, both measured at their actual conditions.

4. The weight of 1 cu. m. of the gas, under its actual conditions.

5. The kilograms of air used to burn 1,000 cu. m. of gas, measured under its actual conditions.

21. A furnace burns the following coal, using 60 per cent excess air:

	Per Cent		Per Cent
C	74.6	O	8.2
H	4.6	H_2O	5.0
N	1.3	Ash	6.3

The ashes from the furnace analyze 20 per cent carbon. The air used is moist, carrying 22 g. of water vapor per cubic meter of dry air.

Required: 1. The cubic meters of dry air theoretically required per kilogram of coal, referred to standard conditions.

2. The cubic meters of moist air actually used, referred to standard conditions

3. The total volume of the flue gases.

4. If the amount of moisture in the air were 22 g of water vapor per cubic meter of *moist* air, what would be the volume of moist air actually used for the combustion of the coal?

22. Coal used in firing a reverberatory furnace analyzed as follows:

	Per Cent		Per Cent
C	65.0	N	2.0
H	5.8	H_2O	4.8
O	10.2	Ash	12.2

The ashes from the furnace amounted to 15 per cent of the coal. 75 per cent excess air was supplied for combustion. The air carried 15 g. of water vapor in each cubic meter of moist air.

Required: 1. The cubic meters of the moist air supplied, per kilogram of coal.

2. The grams of water vapor contained in each cubic meter of the flue gases.

23. A bituminous coal has the following composition

	Per Cent		Per Cent
C	70.6	N	1.4
H	4.8	H_2O	4.6
O	8.6	Ash	10.0

It was burned with 75 per cent excess air. The ashes from the furnace contained 13.6 per cent unburned carbon. The air used was at 15°C., 772 mm. barometric pressure, and carried 11.6 g. of water vapor per cubic meter of dry air measured at standard conditions.

Required: 1. The volume of dry air theoretically required per kilogram of coal, measured at the given conditions.

2. The volume of moist air actually used, and the percentage humidity.

3. The total volume of the chimney gases as they issue from the chimney at a temperature of 420°C.

24. The analysis of a soft coal is as follows:

	Per Cent		Per Cent
C	72.4	O	10.0
N	1.8	H_2O	2.4
H	6.4	Ash	7.0

When this coal was burned in a furnace, using 80 per cent excess air, the ashes averaged 15 per cent unburned carbon. The air used for the combustion carried 12 mm. of water vapor, the barometric pressure being 720 mm.

Required: 1. The total volume of air used (including the moisture content), per kilogram of coal burned.

2. The volume and percentage composition of the products of combustion (flue gases).

3. The weight of the moist air and the total weight of the flue gases of which the volume was determined in requirements 1 and 2.

25. A Pennsylvania coal has the following composition:

	Per Cent		Per Cent
C	80.3	N	1.5
H	4.9	H_2O	2.0
O	3.1	Ash	8.2

When it was used in a furnace, the ashes amounted to 12.1 per cent of the weight of the coal. 30 per cent excess air was used, and the air was three-fourths saturated with water vapor The temperature of the air was 15°C, barometer 740 mm.

Required: 1. The cubic feet of air used, measured dry at standard conditions, per pound of coal.

2. The cubic feet of air used under the actual conditions

3. The volume of the flue gases and the grains of moisture carried in them per cubic foot.

26. Bituminous coal used in a reverberatory furnace analyzed as follows:

	Per Cent		Per Cent
C	75.4	N	1.6
H	6.6	H_2O	2.0
O	7.2	Ash	6.4
S	0.8		

It was burned in a furnace with 60 per cent more air than theoretically required. 4 per cent of the carbon contained in the coal was lost unburned in the ashes.

Required: 1. The cubic meters of air theoretically required per kilogram of coal, measured dry at standard conditions.

2. The cubic meters of moist air used if it were one-half saturated with water vapor and at 22°C., 740 mm. pressure.

3. The cubic meters of flue gases formed in this case

4. The percentage composition of the flue gases.

5. The partial pressure of the water vapor in the flue gases.

27. A crucible furnace for melting aluminum used coke as a fuel. The composition of the coke was:

	Per Cent
C	85
H	1
H_2O	2
Ash	12

The ashes from the furnace were one-fifth unburned carbon. There was used, per kilogram of coke, 12 cu. m. of moist air, measured at standard conditions, carrying 20 mm. of water vapor. Barometer, 720 mm.

Required: 1. The percentage of excess air used.

2. The total volume of the flue gases (wet) and the percentage of free oxygen in them.

3. If the flue gases had contained 6 per cent oxygen, dry analysis, what percentage of excess air would this have indicated?

28. The flue gases from a furnace burning powdered coal were analyzed and found to contain 5.7 per cent free oxygen, wet analysis. The composition of the coal was:

	Per Cent		Per Cent
C	73.6	N	1.7
H	5.3	H_2O	1.4
O	10.0	Ash	8.0

The atmospheric conditions were: temperature, 52°F.; barometer, 28.9 in.; humidity, 68 per cent.

Required: 1. The volume of dry air, in cubic feet at standard conditions, theoretically required per pound of coal.

2. The percentage excess air used.

3. The volume of moist air actually used per pound of coal, measured at the given conditions.

4. The grains of moisture carried per cubic foot of flue gas, and the partial pressure of the water vapor in the flue gases.

29. A coal analyzed as follows:

	Per Cent		Per Cent
C	67.5	N	1.0
H	4.9	H_2O	2.8
O	9.3	Ash	14.5

When burned in a furnace, the flue gas was analyzed and found to contain 11.5 per cent CO_2, dry analysis. The ashes from the furnace carried 18 per cent unburned carbon. Air temperature, 20°C., barometer, 765 mm., saturated with water vapor.

Required: 1. The cubic meters of air, dry, theoretically required per kilogram of coal, measured at standard conditions.

2. The percentage excess air used.

3. The cubic meters of moist air actually used under the given conditions.

4. In making the dry analysis of flue gas, how many grams of moisture were removed per cubic meter of wet flue gas as measured at standard conditions?

30. An open-hearth furnace used coke-oven gas as a fuel. Its analysis was as follows:

	Per Cent		Per Cent
H_2	44.5	C_2H_4	3.0
CO	6.0	C_6H_6	0.8
CO_2	3.0	N_2	8.4
CH_4	34.0	O_2	0.3

20 per cent excess air was used, and the air contained 20 g. of water vapor per cubic meter of moist air.

Required: 1. The cubic meters of moist air used per cubic meter of gas.

2. The volume of the products of combustion, per cubic meter of gas.

3. The grams of water vapor contained in a cubic meter of the products of combustion.

31. The coke-oven gas used in heating the ovens at a coke plant analyzed as follows:

	Per Cent		Per Cent
CO_2	3	C_6H_6	1
CO	6	H_2	44
CH_4	35	N_2	9
C_2H_4	2		

This analysis was made after drying the sample; actually the wet gas was 12 per cent H_2O. The air contained 3 per cent moisture.

The products of combustion from the heating chambers carried 2.6 per cent free oxygen, dry analysis.

Required: 1. The cubic meters of moist air used in burning 1 cu. m. of wet gas.

2. The percentage excess air used.

3. The volume of each constituent of the flue gases.

4. The grams of moisture contained in 1 cu. m. of the flue gases.

32. A coke-oven gas made from Connellsville coal has the following composition:

	Per Cent		Per Cent
C_6H_6	0.8	CO_2	1.2
C_2H_4	3.0	H_2	52.8
CH_4	32.0	N_2	0.4
CO	7.5	H_2O	2.3

It enters the ports of an open-hearth furnace at a temperature of 90°F., pressure 31.90 in. of mercury. It is burned with 25 per cent excess air, the temperature and pressure of which are 1800°F., 31.20 in. The air contains 2 per cent water vapor. The flue gases leave the furnace at 3000°F., 29.60 in.

Required: 1. The cubic feet of dry air theoretically required to burn 1 cu. ft. of gas, both measured at standard conditions.

2. The cubic feet of moist air actually used per cubic foot of gas, both measured at the actual conditions.

3. The percentage composition of the products of combustion, and their total volume as they leave the furnace.

33. A zinc furnace is fired with natural gas analyzing as follows:

	Per Cent		Per Cent
CH_4	83.3	H_2	2.2
C_2H_4	3.2	N_2	1.2
CO	3.4	H_2O	2.6
CO_2	4.1		

The gas was burned in the furnace with 5 per cent more air than required for perfect combustion. Air temperature, 25°C.; barometric pressure, 745 mm.; air two-thirds saturated with water vapor. Gas temperature when burned, 15°C.; pressure, 785 mm.

Required: 1. The cubic meters of dry air theoretically required per cubic meter of gas, both measured at the same conditions.

2. The cubic meters of moist air actually used per cubic meter of gas, both measured at actual conditions.

3. The percentage composition of the flue gases leaving the furnace.

4. The temperature at which water vapor will begin to condense from the flue gases (*i.e.*, saturation temperature for the partial pressure exerted by the moisture in the flue gases)

5. If the flue gases are cooled down to 25°C., what will then be the percentage of water vapor in them, and how many grams of H_2O will have condensed per cubic meter of dry gas (measured at standard conditions)?

34. Coke-oven gas used in firing an open-hearth steel furnace had the following composition:

	Per Cent		Per Cent
CH_4	35	CO	6
C_2H_4	4	O_2	1
H_2	36	N_2	12
CO_2	4	H_2O	2

The products of combustion contained 4.4 g. of moisture (water vapor) in each cubic foot. The air used for combustion carries moisture. 20 per cent excess air was used.

The saturation pressure for water vapor in the air at the temperature used is 26 mm. Barometer, 760 mm.

Required: 1. The volume of dry air (cubic feet) theoretically required for the combustion of 1 cu. ft. of the coke-oven gas.

2. The dry analysis (*i.e.*, excluding all the H_2O content) of the products of combustion.

3. The grams of moisture per cubic foot of the moist air, and the percentage humidity.

35. A Pennsylvania coal has the following composition:

	Per Cent		Per Cent
C	77.20	S	1.42
H	5.10	H_2O	1.45
O	7.22	Ash	5.93
N	1.68		

It is burned with 60 per cent more air than theoretically required. The ashes from the furnace amount to 9.30 per cent of the weight of the coal.

Required. 1. The net calorific power of the coal in Calories per kilogram and in B.t.u. per pound.

2. The cubic meters of air used in combustion, per kilogram of coal.

3. The percentage composition of the flue gases.

4. The moisture content of the flue gases, in grams per cubic meter and in grams per cubic foot.

36. A Pennsylvania coal has the following composition:

	Per Cent		Per Cent
C	76.3	S	2.5
H	4.9	H_2O	2.0
O	3.1	Ash	8.2
N	3.0		

When this was used in a furnace, the ashes contained 14.0 per cent unburned carbon. 30 per cent excess air was used. The temperature of the air was 25°C.; barometer, 740 mm.; partial pressure of moisture in the air, 18 mm.

Required: 1. The practical calorific power of the coal, in B.t.u. per pound, and the percentage of it lost owing to unburned carbon in the ashes.

2. The cubic feet of air theoretically required, measured dry at standard conditions, per pound of coal.

3. The cubic feet of moist air actually used, measured under the given conditions, per pound of coal.

4. The percentage composition of the flue gases, and the grains of moisture carried by them, per cubic foot measured at standard conditions

37. A coal has the following composition:

	Per Cent		Per Cent
C	76.0	O	7.8
H	4.9	H_2O	1.5
S	1.2	Ash	8.6

It is burned on a grate in a furnace used for melting pure copper for casting into ingots. 150 metric tons is melted in 10 hr., using 17 metric tons of coal. The ashes are found to contain 25 per cent unburned carbon. Just melted copper contains 172 Cal. per kilogram. The gases leave the furnace at 1000°C.

Required: 1. The cubic meters of air used per kilogram of coal.

2. The cubic meters of flue gases leaving the furnace per hour, actual conditions.

3. The calorific power of the fuel, per kilogram.

4. The percentage of the original calorific power utilized in melting the copper.

38. A furnace burns 3 metric tons of the following coal:

	Per Cent		Per Cent
C	69.4	O	9.6
H	4.8	H_2O	6.2
N	0.8	Ash	9.2

310 kg. of ashes is made. The gases passing out of the stack are found to amount to 65,200 cu. m. measured at the stack temperature of 230°C. and pressure of 725 mm.

Required: 1. The calorific power of the coal, per kilogram.

2. The percentage of the calorific power of the coal represented by the unburned carbon in the ashes.

3. The cubic meters of air theoretically required to burn the coal, at standard conditions.

4. The percentage excess air used

39. A Bethlehem blast furnace burns in its combustion zone 760 metric tons of coke per day. The coke has the following composition:

	Per Cent
C	88.8
H	1.2
O	0.8
Ash	8.8
Moisture	0.4

In the combustion zone of the blast furnace, conditions are such that the carbon of the coke burns entirely to CO, while the hydrogen does not burn; there is no excess air.

The average atmospheric conditions for the months of January and July, according to the Lehigh University Weather Bureau, were as follows:

January: Temperature, −1°C.; pressure, 754 mm.; humidity, 78 per cent.
July: Temperature, 24°C.; pressure, 747 mm.; humidity, 68 per cent.

Carbon burned to CO develops 2,430 cal. per kilogram.

The moisture in the air is decomposed in the combustion zone of the furnace, absorbing 3,213 Cal. per kilogram.

Required: 1. The cubic meters of blast (air) used per kilogram of coke, if the air is assumed dry at standard conditions.

2. The same, but including moisture and measured at the atmospheric conditions for July.

3. The calorific power of the coke (per kilogram).

4. The percentage of this calorific power that is actually developed in the combustion zone of the furnace.

5. The kilograms of H_2O entering the furnace in the blast per average day, in January and in July.

6. What percentage of the heat developed in the furnace by combustion of the coke was required to decompose this H_2O in each of these months?

7. The percentage composition of the gas resulting from the combustion, in January.

40. A furnace is fired with oil having the following analysis:

	Per Cent
C	84.6
H	10.9
S	0.7
O	3.8

Air is supplied 15 per cent in excess of the theoretical requirement. Specific gravity of the oil, 0.924; degrees Beaumé, 21.5.

Required: 1. The calorific power of the oil, both high and low, in B.t.u. per pound and in Calories per gallon (use Dulong's formula).

2. The calorific power computed from the formula of Sherman and Kropff.

3. The cubic feet of air used, per pound of oil.

4. The percentage of free oxygen in the products of combustion.

41. A furnace uses coke-oven gas of the following composition:

	Per Cent		Per Cent
H_2	37.6	CO	5.6
CH_4	40.8	CO_2	3.7
C_2H_4	4.6	N_2	5.4
C_6H_6	1.2	H_2O	1.1

The gas is burned with 20 per cent excess air. The air carries moisture; assume the humidity to be 40 per cent. The air temperature is 25°C., barometer 730 mm.

Required: 1. The calorific power of the gas, per cubic meter at standard conditions and per cubic meter measured at the atmospheric conditions.

2. The cubic meters of moist air at the given conditions used to burn 1 cu. m. of gas measured at standard conditions.

3. The total volume of the flue gases resulting from the combustion of 1 cu. m. of gas at standard conditions.

42. Producer gas used for firing an open-hearth furnace had the following composition:

	Per Cent		Per Cent
CO	25.4	CH_4	2.1
CO_2	4.4	H_2O	2.9
H_2	17.2	N_2	48.0

It was burned with 10 per cent excess air. The air used carried moisture amounting to 16 grains per cubic foot of moist air. Barometric pressure 750 mm

Required: 1. The calorific power of the gas, per cubic foot.

2. The cubic feet of the moist air used to burn 1 cu. ft. of gas.

3. The percentage composition of the products of combustion.

4. The partial pressure of the moisture in (*a*) the air, (*b*) the products of combustion.

43. Following is the composition of a coal from Newcastle, England (dry analysis):

	Per Cent		Per Cent
C	78.0	S	1.4
H	4.8	N	1.8
O	10.3	Ash	3.7

In addition the coal carries moisture equal to 4.2 per cent of its dry weight. It is burned in a smelting furnace with 60 per cent more air than theoretically required. The ashes from the furnace amount to 4.3 per cent of the coal. The air, assumed dry, is at 20°C., 740 mm pressure.

The flue gases leave the furnace at a temperature of 1000°C.

Required: 1 The calorific power of the coal, dry and wet.

2. The cubic meters of air used to burn the coal, per kilogram of wet coal, at the given conditions.

3. The volume and percentage composition of the flue gases as they leave the furnace.

4. The quantity of heat in Calories per kilogram of wet coal carried out of the furnace in the flue gases.

44. A furnace uses the following coal:

	Per Cent
C	80
H	4
O	8
H_2O	4
Ash	4

The ashes taken from the furnace consist of 3½ parts ash to 1 part carbon

The amount of air supplied was one-sixth more than the theoretical requirement. The air carried moisture to the amount of 25 g. per cubic meter of moist air The gases leave the stack at 600°C.

Required: The percentage of the calorific power of the coal that is carried out of the stack in the hot flue gases.

45. A smelting furnace burns pulverized coal from Illinois, using air 20 per cent in excess of the theoretical requirement, the air containing 1 per cent moisture. The coal analyzes as follows:

	Per Cent		Per Cent
C	54.8	N	1.1
H	3.9	S	3.6
O	8.7	Ash	14.7
H_2O	13.2		

The resulting gaseous products leave the furnace at 2200°F.

Required: 1. The cubic feet of air (moist) used per pound of coal.

2. The volume and percentage composition of the products of combustion

3. The calorific power of the coal.

4. The percentage of the heating value of the coal lost in the hot gases.

5. What proportion of this loss is due to the excess air?

46. A bituminous coal has the following analysis:

	Per Cent
C	68
H	7
O	9
H_2O	4
Ash	12

It is used in firing a reverberatory furnace, and the flue gases pass out of the furnace at a temperature of 1200°C. The air contains 20 g. of moisture per cubic meter of moist air. Assume this moisture passes through the furnace unchanged

In case *a*, the coal is burned with 80 per cent excess air and the ashes amount to 14 per cent of the weight of the coal.

In case *b*, only 40 per cent excess air is used and the ashes are one-third carbon.

Compare, for the two cases, the waste of heat represented by the heating value of the unburned carbon plus the heat carried out in the hot flue gases.

47. A furnace installation is being contemplated, and the economy of various types of furnaces is under consideration. In one of the investigated types natural gas of the following composition is used as fuel, with 10 per cent excess air:

	Per Cent		Per Cent
CO	0.58	C_2H_6	7.92
H_2	29.03	C_2H_4	0.98
CH_4	60.70	N_2	0.79

Type *B* furnace used as fuel bituminous coal of the following composition, with 50 per cent excess air:

	Per Cent		Per Cent
C	73.00	O	9.70
H	5.20	H_2O	3.20
N	1.40	Ash	6.75
S	0.75		

The air used for combustion in each case would contain 35 g. of moisture per cubic meter of moist air, measured at the conditions under which it enters the furnace. The air enters at 20°C., 770 mm.

Required: 1. How many kilograms of coal are necessary to furnish the same heating value to the process as 1 cu. m. of gas, disregarding heat contained in the air?

2. Calculate the amounts of air (actual conditions) required by each process to obtain the same heating value as in requirement 1.

3. If the flue gases from the gas furnace enter the stack at 1000°C., how will the loss of heat in these flue gases compare with the calorific power of the gas burned? Also, how will the heat loss in the stack gases compare with the calorific power in the case of the coal furnace?

48. Pulverized coal used in a reverberatory furnace analyzed as follows:

	Per Cent
C	68.8
H	6.4
O	8.4
H_2O	3.2
Ash	13.2

The coal is burned with 40 per cent excess air. Assume that the coal enters the furnace at 0°C., the air at 60°C. The products of combustion leave the furnace at 1200°C.

Assume the mean specific heat of SiO_2 to be $0.18 + 0.00008t$.

Required: 1. The practical calorific power of the coal.

2. The heat supplied to the furnace, per kilogram of coal.

3. The percentage of this heat that is carried out of the furnace in:

a. The products of combustion exclusive of the excess air.

b. The excess air

c. The ash. (Assume the ash to be SiO_2 and to leave at the same temperature as the gases.)

4. If the furnace burns 2.5 metric tons of coal per hour, what boiler horsepower can be developed by passing the gases through waste-heat boilers having a thermal efficiency of 65 per cent?

49. An open-hearth furnace burns producer gas having the following composition, using 9,000 cu. m. of gas per hour (measured at 300°C.):

	Per Cent		Per Cent
CO	22.0	CH_4	3.3
CO_2	5.7	H_2O	2.6
H_2	10.5	N_2	55.9

The gas is burned with 20 per cent more air than theoretically required. It enters the ports of the furnace at a temperature of 300°C., and the air used to burn it enters at 800°C.

Required: 1. The cubic meters of air used to burn 1 cu. m. of gas, both measured at the temperature given.

2. The percentage composition of the flue gases

3. The calorific power of the gas in Calories per cubic meter and in B.t.u. per cubic foot.

4. The quantity of heat supplied to the furnace per minute, in Calories.

50. A natural gas from Galveston, Tex., contains by analysis the following.

	Per Cent		Per Cent
CH_4	92	CO_2	0.27
H_2	2.2	H_2S	0.10
C_2H_4	0.50	O_2	0.24
CO	0.56	N_2	4.13

The gas is used as fuel in an open-hearth steel furnace. The air supplied for combustion is at a pressure of 780 mm., a temperature of 40°C., and contains 1.5 per cent moisture. 10 per cent excess air is used. The flue gases enter the stack at 500°C.

Required: 1. The volume of moist air actually used under given conditions for the combustion of 1 cu. m. of gas measured at standard conditions.

2. The volume of the products of combustion per cubic meter of gas burned (standard conditions).

3. The calorific power of the gas, and the heat lost in the outgoing gases.

4. If the air were preheated to 1000°C., what would be the total heat input to the furnace per cubic meter of natural gas burned?

51. Powdered coal used in a cement kiln has the following composition:

	Per Cent		Per Cent
C	73.6	O_2	10.0
H_2	5.3	Ash	8.5
N_2	1.2	H_2O	0.6
S	0.8		

Required: 1. The calorific power of the coal, both high (calorimetric) and low (practical).

2. The calorific intensity, if completely burned with the theoretical requirement of air.

3. If the coal is burned with excess air, and the products of combustion are found on analysis to contain 4.5 per cent free O_2, what percentage of excess air is used?

4. What is the calorific intensity in this case?

52. Coke analyzes as follows:

	Per Cent
C	89.5
H	1.1
Ash	9.4

Required: The theoretical maximum temperature of the flame when the coke is burned:

a. Under theoretical conditions.
b. With 50 per cent excess air.
c. With 10 per cent excess air, the air preheated to 1000°C.

53. Following is the composition of a California crude oil:

	Per Cent
C	81.52
H	11.01
S	0.55
O	6.12
N	0.80

The specific gravity is 0.966. It is burned with 8 per cent excess air, the air carrying 21 g. of water vapor per cubic meter of dry air.

Required: 1. The low calorific power of the oil, in Calories per kilogram and in B.t.u. per gallon.

2. The theoretical maximum flame temperature when burned.

54. Producer gas analyzes as follows:

	Per Cent		Per Cent
CO	25.2	CH_4	4.0
H_2	15.3	H_2O	2.9
CO_2	5.0	N_2	47.6

Required: 1. The theoretical calorific intensity of this gas.

2. The theoretical flame temperature if the gas is burned with 50 per cent excess air, without preheating.

3. The same, if burned with 10 per cent excess air, both air and gas being preheated to 1000°C.

55. The natural gas of Findlay, Ohio, analyzes:

	Per Cent
CH_4	93.35
H_2	1.64
C_2H_4	0.35
N_2	4.66

It is burned with air (assumed dry) preheated in regenerators to 500°C.; 5 per cent excess air is used.

Required: 1. The calorific intensity as burned.

2. How much higher is the flame temperature than it would have been without preheating the air?

3. If used in a steel furnace where the maximum flame temperature required is 2100°C., to what temperature must the air be preheated to attain this temperature?

56. A blast-furnace gas used for fuel contains 30 per cent CO, 14 CO_2, 2 CH_4, and 54 N_2. Allow 10 per cent excess air for combustion.

Required: 1. The maximum theoretical temperature obtainable without preheating.

2. The temperature to which the gas and air would have to be preheated to yield a flame temperature of 3300°F., assuming both preheated to the same temperature.

57. The producer gas of Prob. 49 is used for fuel in an open-hearth furnace. It is burned with 15 per cent excess air, the air being assumed dry. The regenerators preheat both the air and the gas to a temperature of 500°C.

Required: 1. The temperature attained by the combustion.

2. The temperature which would have been obtained if the furnace had no regenerators, air and gas being assumed to enter the ports cold.

3. To what temperature would the gas have to be preheated in order to yield the same temperature as under requirement 1, without preheating the air?

58. A reverberatory refining furnace uses oil containing 86 per cent C, 14 per cent H, having a calorific power of 10,932 Cal. per kilogram. The gases leaving the furnace analyze 75 per cent N_2, 10.3 CO_2, 10.1 H_2O, 4.6 O_2 and have a temperature of 1200°C. They pass from the furnace into a waste-heat boiler, which operates at an efficiency of 60 per cent. They leave the boiler at 400°C.

Required: 1. The total volume of gas leaving the furnace, per kilogram of oil burned, measured at 1200°C.

2. The percentage of the calorific power of the oil that is carried out of the furnace by the gases.

3. The kilograms of water evaporated in the boiler, per kilogram of oil burned, at the equivalent of 539 Cal. required to evaporate 1 kg.

4. The percentage of heat dropped by the gases in passing through the boiler that is utilized in making steam.

59. A regenerative open-hearth furnace uses producer gas as fuel. The gas is burned with 10 per cent excess air. The temperature of the air and gas just before combustion averages 800°C., while the temperature at the entrance to the checkers averages 1400°C., and at their exit 600°C. From the checkers, the flue gases pass to the chimney.

The composition of the gas is as follows:

	Per Cent		Per Cent
CO	22	CH_4	2
CO_2	8	H_2O	4
H_2	11	N_2	53

Required: 1 The theoretical average temperature of the flame.

2. The efficiency of regeneration.

3. The percentage of the total heat entering the furnace which is lost in the chimney gases, and the amount of this percentage if the checkers were not used.

60. A blast-furnace gas is composed as follows.

	Per Cent
CO	24
CO_2	13
H_2	2
H_2O	4
N_2	57

It is burned in a regenerative furnace melting down iron, using the theoretical requirement of air, which contains 2 per cent moisture, both gas and air being preheated to 600°C., and yielding a combustion temperature of 1600°. For every 200 kg. of iron melted, 1,000 cu. m. of gas is burned. The heat in the iron at the temperature of the bath is 350 Cal. per kilogram. At the flue end of the furnace (entrance to the checkers) the temperature has dropped to 1100°, at the exit from the checkers to 500°.

Required: 1. The percentage of the original available heat which was lost in combustion, the percentages of the same utilized and lost in the furnace proper, the percentages utilized and lost in the checkers, and the percentage lost in the stack gases.

2. The thermal efficiencies of the furnace proper and of the checkers

61. An open-hearth steel furnace of the Bethlehem Steel Co is fired with coke-oven tar composed as follows:

	Per Cent		Per Cent
C	87 8	N	1 1
H	5 6	S	0 6
O	2 2	H_2O	2 7

The specific gravity of the tar is 1.14

The tar at the burner has a temperature of 190°F. and is atomized with 0.42 lb. of steam per pound of tar. The temperature of the steam is 550°F The preheated air for combustion (assumed dry) enters the ports at 1900°F

The products of combustion contain 1.5 per cent oxygen, dry analysis They leave the furnace and enter the checkers at 2750°F

Assume the specific heat of the tar to be 0.24.

Required: 1. The net calorific power of the tar, in B t u per gallon

2. The cubic feet of dry air at standard conditions used per pound of tar, and the percentage excess air, assuming that all the combustion is by air (*i.e.*, disregard combustion by steam).

3. The total heat supplied to the furnace per pound of tar burned

4. The heat carried out of the furnace by the hot gases, including the steam with these gases but disregarding gases resulting from the charge in the furnace.

5. The efficiency of regeneration by the checkers, considering only the heat in the gases as in requirement 4 and assuming that the checkers heat the incoming air to 1900°F.

6. The theoretical maximum temperature of the flame at the burners.

62. An open-hearth furnace is fired with crude oil from Texas, analyzing as follows:

	Per Cent
C	84.6
H_2	10.9
O_2	2.9
S	1 6

The specific gravity is 0.90. 20 per cent excess air is used.

The products of combustion leave the furnace and enter the regenerators at 1600°C. They leave the regenerators and enter the waste-heat boiler at 700°C. They leave the boiler and enter the stack at 200°C.

The regenerators preheat the air to 1000°C. The boiler develops ¼ boiler hp. per kilogram of oil burned per hour.

Required: 1. The calorific power of the oil, in Calories per kilogram, by Dulong's formula.

2. The calorific power of the oil, in B.t.u. per gallon.
3. The heat given up by the products of combustion, per kilogram of oil burned:
   a. In the furnace proper.
   b. In the regenerators.
   c. In the boiler.
   d. Lost to the stack.
4. The efficiency of the regenerators and of the boiler.

63. Coke used as fuel in a crucible pot furnace analyzed as follows:

	Per Cent
C	85 8
Ash	9 8
H_2O	4 4

Less air was supplied than theoretically required. 5 per cent of the carbon of the coke was lost in the ashes, and 16 per cent of the carbon burned went to CO instead of CO_2.

The air used was moist, carrying 22 g. of water vapor in each cubic meter of moist air. This moisture burns carbon according to the reaction:

$$C + H_2O = CO + H_2,$$

the H_2 remaining unoxidized

Required: 1. The volume of the moist air used, per kilogram of coke.

2. The volume of the flue gases, per kilogram of coke
3. The calorific intensity:
   a. If the coke were burned completely with dry air.
   b. If burned under the conditions stated above.

CHAPTER IV

MANUFACTURE OF COKE AND PRODUCER GAS

If coal is heated out of contact with air, it cannot oxidize or burn. It will, however, partly decompose, and volatile matter contained in it will be expelled in gaseous form. The volatile matter will consist of various hydrocarbon gases (such as CH_4, C_2H_4, C_6H_6), hydrogen, tar, ammonia, light oils, and moisture. The residue will consist of fixed carbon and ash, together with some volatile matter not completely expelled. The amount of volatile matter expelled depends on the composition of the coal and the temperature to which it is heated. When the process is carried on in a by-product coke oven, the residue is coke, and the volatile matter is led through pipes, condensers, etc., to separate its various constituents and recover them as by-products.

If the coal is heated and some air admitted, but less than the amount required for complete combustion, much the same action occurs as above and in addition there is partial oxidation of the volatile matter, the fixed carbon, or both. Most of the carbon oxidized forms CO instead of CO_2. The net result depends on whether the air is admitted above the bed of coal, where it can burn mainly the volatile matter, or beneath the bed of coal, passing up through it and burning mainly the fixed carbon (chiefly to CO). The former action takes place in the old-fashioned beehive coke oven, now very little used. The volatile matter is largely burned and goes to waste; but the residue is not burned except a little at the surface, and thus coke results. The latter action is of much greater importance and is carried on extensively in gas producers. It results in unburned volatile matter (though less of it) and a large amount of CO, which mix and together with other constituents form a valuable combustible gas, produced in this manner for use as fuel.

Production of Coke and By-products.—Consider the coking process applied to a coal having the following analysis (coal of Example 3):

	Per Cent		Per Cent
C	79 1	S	0.9
H	6 9	H_2O	1 8
O	6 6	Ash	3 3
N	1 4		

Consider the products of the coking process to be coke, coke-oven gas, ammonia, and tar. Other by-products will be disregarded, being obtained later by further treatment of the gas or tar, processes in which the metallurgist is not directly interested. The 79.1 per cent of carbon in the coal is partly in the volatile matter as hydrocarbon compounds and partly fixed carbon. It will be divided among the coke, the coke-oven gas, and the tar. The hydrogen will likewise be divided, though the amount left in the coke will be small and is sometimes neglected. The oxygen is combined in the coal along with hydrogen, but during the coking process some of it forms CO and CO_2 because of reactions like the following:

$$C + H_2O = CO + H_2.$$
$$C + 2H_2O = CO_2 + 2H_2.$$

A little oxygen remains in the coke, and most of the rest goes into the gas as H_2O. There will be some air in the coke oven when it is closed, surrounding the pieces of coal and filling void spaces; most of its oxygen will behave the same as the oxygen in the coal. The amount of it, however, is small, and it is often neglected. There is also the possibility of leakage. Nitrogen in part forms ammonia (NH_3); as this compound is unstable at the higher temperatures, much of the nitrogen will enter the gas as free N_2. It is probably best to assume that all the sulphur gasified forms H_2S, the total being small, though SO_2 and S vapor are possibilities. Some sulphur will remain in the coke. Water evaporates quickly and enters the gas as water vapor. The ash remains entirely in the coke.

A determination of the percentage of ash in the coke at once fixes the weight of coke obtained from a ton of the coal charged into the oven, for we may write:

$$\text{Wt. of ash in coal} = \text{wt. of ash in coke.}$$

Let the coke here analyze 4.7 per cent ash. Then, using 1,000 kg. as a metric ton of coal:

$$0.033 \times 1{,}000 = 0.047 \times \text{wt. of coke.}$$
$$\text{Wt. of coke} = \frac{0.033}{0.047} \times 1{,}000 = 700 \text{ kg.}$$

Let the complete analysis of the coke be as follows:

	Per Cent		Per Cent
C	93.0	N	0.4
H	0.8	S	0.6
O	0.5	Ash	4.7

The 700 kg. of coke contains 0.93 × 700 = 651 kg. of carbon. Carbon in the gas and in the tar is therefore 791 − 651 = 140 kg. Let the tar obtained from a ton of coal be 40 kg., 90 per cent carbon and 7 per cent hydrogen. Then, 140 − 36, or 104 kg. of carbon will be contained in the coke-oven gas. From this total carbon content of the gas and the analysis of the gas, the volume of gas yielded may be calculated. The method employed is a very common one in metallurgical calculations. It is used in connection with producer gas, blast-furnace gases, roasting, smelting, etc., wherever the *percentage composition of a gas is known*, so that the weight of one of the elements (usually C or S) contained in one unit volume of the gas can be compared with the total weight of that element in the entire volume of gas.

Let the analysis of the coke-oven gas (by volume, dry analysis) be as follows:

	Per Cent		Per Cent
H_2	56.9	CO	4.6
CH_4	28.5	CO_2	2.1
C_2H_4	3.0	NH_3	1.2
C_6H_6	0.9	N_2	2.8

To find the weight of carbon (in kilograms) contained in 1 cu. m. of this gas: The volume of CH_4 is 0.285 cu. m.; and since 22.4 cu. m. of CH_4 contains 12 kg. of C, 1 cu. m. of CH_4 contains $\frac{12}{22.4}$ kg. of C,* and the CH_4 present contains $0.285 \times \frac{12}{22.4} = 0.153$ kg. of C. Similarly, the C_2H_4 (which has two atoms of C) will contain $0.03 \times 2 \times \frac{12}{22.4} = 0.032$ kg. of C. We proceed in this manner with all the carbon-bearing constituents of the gas. The work can be done most expeditiously by adding the percentages first, thus:

Kilograms of C in $CH_4 = 0.285 \times \frac{12}{22.4}$.

In $C_2H_4 = 2 \times 0.03 = 0.06$

In $C_6H_6 = 6 \times 0.009 = 0.054$

In $CO = 0.046$

In $CO_2 = \underline{0.021}$

Total $= 0.466 \times \frac{12}{22.4} = 0.250$ kg. of C per cubic meter of the coke-oven gas

From the relation

Wt. of C in 1 cu. m. of gas × cu. m. of gas = total C in gas, we have:

$$\text{Cu. m. of gas} = \frac{\text{total wt. of C}}{\text{wt. of C in 1 cu. m.}}$$

$$= \frac{104}{0.250} = 416 \text{ cu. m.,}$$

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* The factor $\frac{12}{22.4}$ is so often used that it may be found convenient to memorize its value, 0.536.

the volume of gas (dry) made per ton of coal. (This is the volume at standard conditions, since it depends on the factor 22.4.)

It may be instructive to check up on the distribution of the hydrogen originally contained in the coal among the resulting products. The coke-oven gas contains per cubic meter 0.569 cu. m. of free H_2. Since 1 volume of CH_4 represents 2 volumes of H_2, 0.285 cu. m. of CH_4 contains 0.57 cu. m. of H_2. Thus:

Free H_2: $1 \times 0.569 = 0.569$ cu. m.
H_2 in CH_4: $2 \times 0.285 = 0.57$
H_2 in C_2H_4: $2 \times 0.03 = 0.06$
H_2 in C_6H_6: $3 \times 0.009 = 0.027$
H_2 in NH_3: $1.5 \times 0.012 = 0.018$
Total $= 1.244$ cu. m. of H_2 represented in each cubic meter of coke-oven gas. Then the total hydrogen in the 416 cu. m. of gas per ton of coal is:

$1.244 \times 416 = 518$ cu. m. $= 46.6$ kg.
In the tar: $0.07 \times 40 = 2.8$
In the coke: $0.008 \times 700 = 5.6$
Total hydrogen accounted for $= 55.0$ kg.

The coal contained 69 kg. of hydrogen. The difference may be assumed to have gone into the gas as H_2O and H_2S, neither of which has been separated in the analysis of the gas. A very close check, however, cannot be expected, owing to inaccuracies in the analyses, etc. An attempt to check up on the oxygen and the nitrogen is particularly uncertain because these elements are present in small amounts which may be overshadowed by presence of air not allowed for and because the nitrogen content is difficult to determine analytically, being usually obtained "by difference."

The calorific power of the coke, by Dulong's formula, is:

$$8{,}100 \times 0.93 + 34{,}000\left(0.008 - \frac{0.005}{8}\right) + 2{,}200 \times 0.006$$
$$-586(9 \times 0.008) = 7{,}533 + 252 + 13 - 42 = 7{,}756 \text{ Cal.}$$

The calorific power of the coal (see p. 26) is 8,119 Cal. The percentage of the original heating value of the coal represented in the coke is therefore

$$\frac{0.700 \times 7{,}756}{8{,}119} = 66.8 \text{ per cent.}$$

The calorific power of the gas is 4,825 Cal. per cubic meter. The percentage of the heating value of the coal present in the gas is, therefore,

$$\frac{0.416 \times 4{,}825}{8{,}119} = 24.7 \text{ per cent.}$$

Producer Gas.—In the gas producer the air enters at the bottom and passes upward through a deep bed of fuel. The oxygen is consumed in burning carbon, chiefly according to the reaction

$$\mathrm{C + O_2 = CO_2}. \qquad (1)$$

The bed of hot fuel must extend several inches above the point at which this reaction occurs. The CO_2 which has been formed is then reduced to CO by hot carbon as it passes upward:

$$\mathrm{CO_2 + C = 2CO}. \qquad (2)$$

When reactions (1) and (2) are added, the result is:

$$\mathrm{2C + O_2 = 2CO}. \qquad (3)$$

This may be taken as the principal reaction of the producer in calculating the composition of the gas formed. The object is to form CO from the carbon instead of CO_2; the products of combustion then contain the combustible CO and can be used as a fuel gas. In this theoretical form, the combustion of 24 kg. of carbon yields 44.8 cu. m. of CO, which would have mixed with it the nitrogen of the air. The 22.4 cu. m. of oxygen required would be accompanied by $22.4 \times {}^{79}/_{21} = 84.3$ cu. m. of nitrogen. The total volume of the producer gas would be 129.1 cu. m., or 5.38 cu. m. per kilogram of carbon burned, and it would be composed of 34.7 per cent CO and 65.3 per cent N_2.

The combustion of carbon to CO generates 2,430 Cal. per kilogram of carbon. But the gas producer is not a device for heating, and a great deal of unwanted heat is thus produced. A producer of large size, which loses or dissipates less heat in proportion to the amount of coal it burns than a small producer, would become much overheated. The excess heat can be absorbed and at the same time the gas produced can be greatly enriched by the device of feeding steam to the producer along with the air. The steam will burn hot carbon in accordance with the reaction

$$\mathrm{C + H_2O = CO + H_2}. \qquad (4)^*$$

In this reaction the oxidation of carbon to CO, of course, generates the same amount of heat as though it were burned by air, but the accompanying decomposition of the steam absorbs heat. The decomposition, as the reaction shows, liberates hydrogen, and it absorbs an amount of heat equal to the heat generated when hydrogen is burned to H_2O (vapor) This will be seen in the table of heats of formation (Table XLII, page 414) to be 28,680 Cal. per kilogram of hydrogen, equivalent to 3,210 Cal. per kilogram of steam and to 4,820 Cal. per kilogram of carbon oxidized in reaction (4). The reaction as a whole, therefore, absorbs 4,820 − 2,430 = 2,390 Cal. per kilogram of carbon. Thus the amount of steam fed is made just equal to the amount required to absorb the excess heat generated. Too much steam would lower the temperature too much and eventually extinguish the fire.

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* Some of the carbon and steam will react according to the equation $\mathrm{C + 2H_2O = CO_2 + 2H_2}$, this reaction increasing relatively as the temperature of the carbon decreases. The temperature in the producer is ordinarily kept high enough to minimize its occurrence, and consequently it may usually be neglected.

Reaction (4) shows that burning carbon with steam introduces combustible hydrogen in the producer gas, whereas burning with air introduces inert nitrogen. The heating value added to the gas is the calorific power of the hydrogen, and this is equal to the heat absorbed in decomposition of steam. The gas is further enriched *per unit volume,* because the volume of the hydrogen is less than the volume of the nitrogen.

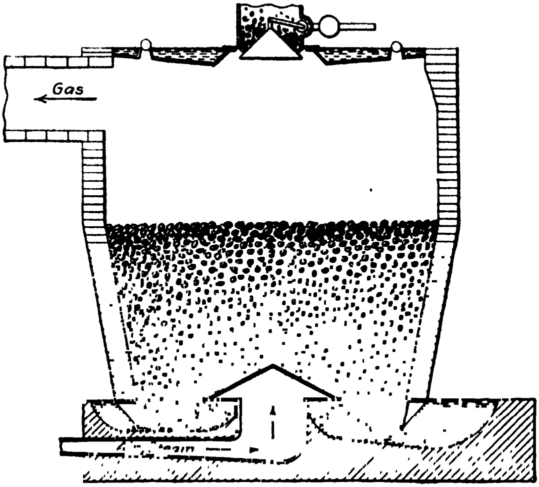

Fig. 2.—Sectional view of a gas producer.

In addition to the burning of carbon by steam in the producer, the calculation must often take account of certain other factors which enter into the operation in practice. First there is the fact that not all the steam injected will enter into the reaction; some of it passes through without being decomposed and occurs as water vapor in the gas produced. Likewise, not all the CO_2 formed in reaction (1) will be reduced to CO; some of it will pass through and cause a considerable percentage of CO_2 in the gas produced. The coal is fed from the top of the producer and heats gradually without access of air, all of which has been consumed in the bottom (see Fig. 2). Consequently, it is subjected to conditions similar to those in the coke oven, so that much of its volatile matter is expelled and goes to enrich the gas produced. Moisture in the coal evaporates and enters the gas as such. Moisture in the air behaves the same as the steam.

Summarizing, the producer gas will be made up of the following constituents, all of which can be calculated when the analysis of the fuel is known and the facts are known as to the amounts of air and steam used, the amount of steam undecomposed, the division of the carbon between CO_2 and CO, and the amount ot volatile matter expelled. In the absence of part of these data, useful approximations can still be made by calculation, particularly if reasonable assumptions can be made to take the place of missing data. The constituents are:

Volatile matter, principally hydrocarbons, H, CO, H_2O.
CO from combustion of carbon by air and by steam.
CO_2 from combustion of carbon, chiefly by air.
H from decomposition of steam.
N from air and some from the fuel
H_2O from undecomposed steam and from moisture of the fuel.

Before this calculation is taken up, it will be profitable to perform certain calculations applicable when the compositions of the coal and of the gas produced are both known. This affords a simple problem and one similar to that already met with in the discussion of the coke-oven process. Let the composition of the coal be the same as there used (page 53), and let the composition of the gas be as shown in the second column below.

	Coal, Per Cent
C	79.1
H	6.9
O	6.6
N	1.4
S	0.9
H_2O	1.8
Ash	3.3

	Gas, Per Cent
CO	25.2
CO_2	4.8
H_2	16.0
CH_4	3.6
C_2H_4	3.2
SO_2	0.1
H_2O	2.4
N_2	44.7

Let it be required to find, per kilogram of coal used, (1) the cubic meters of gas produced, (2) the cubic meters of air used, (3) the kilograms of steam blown in, and (4) the kilograms of steam utilized in burning carbon.

Assume that the ashes from the producer amount to 4 per cent of the weight of the coal. Then, the unburned carbon contained in them is $0.04 - 0.033 = 0.007$ kg. per kilogram of coal. The weight of the coal that is gasified then is $0.791 - 0.007 = 0.784$ kg.

One cubic meter of the gas contains $(0.252 + 0.048 + 0.036 + 2 \times 0.032) \frac{12}{22.4} = 0.214$ kg. of carbon.

The volume of gas is, therefore, $\frac{0.784}{0.214} = 3.66$ cu. m. per kilogram of coal (1).

The nitrogen in the gas may be used to find the volume of air, since it could have come from only two sources—the air and the coal. The amount in the gas is $0.447 \times 3.66 = 1.635$ cu. m. The amount in the coal is $0.014 \times \frac{22.4}{28} = 0.011$ cu. m. Therefore, the amount in the air is $1.635 - 0.011 = 1.624$ cu. m., and the volume of air is $\frac{1.624}{0.79} = 2.06$ cu. m. (assumed dry) (2).

In a similar manner the hydrogen in the gas may be used to find the amount of steam used. As some of the hydrogen from the steam may form hydrocarbons, it will be best to take the entire amount of hydrogen represented in the gas, whether free or combined. From this, the entire amount of hydrogen in the coal is deducted, the difference being hydrogen from steam. In the gas there is:

$$\begin{aligned} \text{Free } H_2 &= 0.160 \text{ cu. m.} \\ H_2 \text{ in } CH_4 = 2 \times 0.036 &= 0\ 072 \quad (\text{since } CH_4 = C + 2H_2) \\ H_2 \text{ in } C_2H_4 = 2 \times 0.032 &= 0.064 \\ H_2 \text{ in } H_2O = 1 \times 0.024 &= \underline{0\ 024} \\ \text{Total} &= 0\ 320 \times 3\ 66 = 1\ 17 \text{ cu. m.} \end{aligned}$$

$$1.17 \text{ cu. m. } H_2 \times \frac{2}{22.4} = 0.1045 \text{ kg. H.}$$

In the coal:

$$H = 0.069 + (\tfrac{2}{18} \times 0.018) = 0.071 \text{ kg.}$$

$$H \text{ from steam} = 0.1045 - 0.071 = 0.0335 \text{ kg.}$$

$$\text{Weight of steam used} = \tfrac{18}{2} \times 0.0335 = 0.302 \text{ kg. (3).}$$

The H_2O in the gas minus the H_2O received by evaporation of the moisture of the coal represents undecomposed steam.

H_2O in the gas $= 0.024 \times 3.66 = 0.0879$ cu. m.

$0.0879 \times \frac{18}{22.4} = 0.0707$ kg.

$0.0707 - 0.018 = 0.053$ kg. of steam not decomposed.

Steam utilized in burning carbon $= 0.302 - 0.053 = 0.249$ kg., or 83 per cent of the amount blown in (4)

The volume of air used (requirement 2) might be obtained from the oxygen instead of the nitrogen, after calculating the steam, which also contains oxygen. This may now be done as a check on the result obtained by the nitrogen method:

$$\text{Total } O_2 \text{ in gas} = \left(\frac{0.252}{2} + 0.048 + 0.001 + \frac{0.024}{2}\right) 3.66 = 0.684 \text{ cu. m.}$$

$$\text{Total } O_2 \text{ in coal and steam} = 0.066 + \tfrac{16}{18} \times 0.018 + \tfrac{16}{18} \times 0.302 = 0.350 \text{ kg.}$$
$$= 0.245 \text{ cu. m.}$$

O_2 from air = 0.684 − 0.245 = 0.439 cu. m.

Volume of air = $\frac{0.439}{0.21}$ = 2.09 cu. m., compared with 2.06 cu. m., the result obtained from the nitrogen content.

The problem of calculating the volume and composition of the gas produced from a given coal will now be considered. It is necessary that the amount of air and steam used, or at least the ratio between them, or the percentage of the total carbon which each burns be known. It is also necessary to know what proportion of the carbon goes to CO and to CO_2; it may usually be assumed that all the carbon burned by steam forms CO, but the division of the carbon burned by air must be specified. The proportion of the steam passing through, undecomposed, must also be known. With these data in hand, the calculation proceeds along the lines of calculation of the products of combustion in an ordinary combustion problem such as Example 3. The details will appear in the example given below, in which the composition of the coal used has again been taken the same as that of Example 3.

Example 6

The coal used in a gas producer analyzed as follows:

	Per Cent		Per Cent
C	79.1	S	0.9
H	6.9	H_2O	1.8
O	6.6	Ash	3.3
N	1.4		

The producer is fed with a mixture of air and steam in the proportion of 8 cu. m. of air (moist) to 1 kg. of steam. Only 85 per cent of the steam is decomposed. The air carries 12 mm. of water vapor. The ashes contain carbon equal to 2 per cent of the coal. Of the 79.1 per cent carbon in the coal, 65 per cent represents fixed (nonvolatile) carbon, and 14.1 per cent is contained in volatile matter, which may be assumed to enter the gas as CH_4. Of the carbon burned by air, one-fifth goes to CO_2, four-fifths to CO.

Required: 1. The percentage of the fixed carbon burned by air and by steam.

2. The volume of gas produced per kilogram of coal.

3. The percentage composition of the gas.

4. The percentage of the heat generated by oxidation of carbon which is absorbed by decomposition of steam.

Solution: The 8 cu. m. of moist air contains $\frac{12}{760} \times 8.0$ = 0.126 cu. m. of water vapor = 0.101 kg. Assume this is decomposed in the same proportion as the steam. The mixture fed then consists of:

7.874 cu. m. of dry air and 1.101 kg. of H_2O, of which 0.936 kg. of H_2O is decomposed.

0.21 × 7.874 = 1.654 cu. m. of O_2 in the air. How much carbon will this oxidize when one-fifth goes to CO_2, four-fifths to CO?

One-fifth in the reaction $C + O_2 = CO_2$ (*a*).

Four-fifths in the reaction $2C + O_2 = 2CO$ (*b*).

These two reactions may be added in such proportions as to make four atoms of C in (*b*) to one atom in (*a*); therefore (*b*) should be multiplied through by 2, giving $4C + 2O_2 = 4CO$. Adding this to (*a*) gives $5C + 3O_2 = CO_2 + 4CO$, an equation which represents the combustion of carbon in the proportions stated. If 1.654 cu. m. of O_2 is used in this reaction, the weight of carbon oxidized is $1.654 \times \frac{60}{3 \times 22.4} = 1.476$ kg.

How much carbon will be oxidized by the 0.936 kg of H_2O? The reaction is $C + H_2O = CO + H_2$.

C oxidized $= 0.936 \times {}^{12}\!/_{18} = 0.624$ kg.

Therefore the mixture fed burns 1 476 kg of C by air while 0 624 kg of C is burned by steam (the moisture in the air being counted as steam) Then, $\frac{1.476}{2.100} = 70$ 4 per cent is burned by air, 29.6 per cent by steam (1)

The carbon lost in the ashes must be deducted from the fixed carbon to obtain the amount oxidized, as follows: $65 - 2 = 63$ per cent, or 0.63 kg. of C is oxidized per kilogram of coal. Some of this will be oxidized by the 0.066 kg of O in the coal, the rest will be oxidized by air and by steam in the ratio just determined Although it is not stated in what ratio the 0.066 kg. of O in the coal forms CO and CO_2, it is most reasonable to assume that it does so in the same ratio as the oxygen of the air. We must also allow some oxygen for burning the S to SO_2. (The hydrogen of the coal will not oxidize, since the excess of hot carbon in the producer causes the reaction $H_2O + C = CO + H_2$.)

0.009 kg. of S requires $0.009 \times {}^{32}\!/_{32} = 0.009$ kg. of O This leaves $0.066 - 0\ 009 = 0.057$ kg. of O, which oxidizes C according to the reaction $5C + 3O_2 = CO_2 + 4CO$. C oxidized $= 0.057 \times {}^{60}\!/_{96} = 0.036$ kg This leaves $0\ 63 - 0\ 036 = 0.594$ kg. of C burned by air and steam, of which $0.704 \times 0.594 = 0.418$ kg. is burned by air and $0.296 \times 0.594 = 0.176$ kg. is burned by steam.

From the air reaction, 0.418 kg. of C requires $0\ 418 \times \frac{67\ 2}{60} = 0\ 468$ cu m. of O_2 and forms ${}^{1}\!/_{3} \times 0.468 = 0.156$ cu. m. of CO_2 and $4 \times 0.156 = 0.624$ cu m of CO. N_2 accompanying this O_2 in the air is ${}^{79}\!/_{21} \times 0\ 468 = 1.760$ cu. m

From the steam reaction, 0.176 kg. of C requires $0\ 176 \times \frac{22.4}{12} = 0.329$ cu m of H_2O and forms 0.329 cu. m. of CO and 0.329 cu m of H_2

The steam thus used is only 85 per cent of the steam blown in. The volume of undecomposed steam, which enters the producer gas as H_2O (vapor), is therefore ${}^{15}\!/_{85} \times 0.329 = 0.058$ cu. m.

$$N_2 \text{ from the coal} = 0.014 \times \frac{22.4}{28} = 0\ 011 \text{ cu m.}$$

$$\text{Volume of the } SO_2 = 0.009 \times \frac{22\ 4}{32} = 0\ 006$$

$$H_2O \text{ from the coal} = 0.018 \times \frac{22.4}{18} = 0.022$$

$$0.141 \text{ kg. of C forms } CH_4. \quad 0.141 \times \frac{22.4}{12} = 0.263 \text{ cu m. of } CH_4.$$

This contains $2 \times 0.263 = 0.526$ cu. m. of H_2. The coal contained 0.069 kg. of H, or 0.773 cu. m. Therefore, $0.773 - 0\ 526 = 0.247$ cu. m. is expelled and enters the gas as free hydrogen.

Summary of gas produced:

$$\begin{aligned}
CO &= 0.621 + 0.329 = 0.953 \text{ cu m} &&= 25.0 \text{ per cent}\\
CO_2 &= 0.156 &&= 4.1\\
H_2 &= 0.329 + 0.247 = 0.576 &&= 15.1\\
CH_4 &= 0.263 &&= 6.9\\
SO_2 &= 0.006 &&= 0.2\\
H_2O &= 0.022 + 0.058 = 0.080 &&= 2.1\\
N_2 &= 1.760 + 0.011 = 1.771 &&= 46.6\\
\text{Total volume of producer gas} &= 3.805 \text{ cu m} && 100.0 \text{ per cent (2 and 3)}
\end{aligned}$$

$$\text{Heat generated by } C \rightarrow CO_2 = \frac{12}{22.4} \times 0.156 \times 8{,}100 = 677 \text{ Cal}$$

$$\text{Heat generated by } C \rightarrow CO = \frac{12}{22.4} \times 0.953 \times 2{,}430 = 1{,}241$$

$$\text{Total heat from combustion of carbon} = 1{,}918 \text{ Cal}$$

$$\text{Heat absorbed by decomposition of steam} = 0.329 \times \frac{18}{22.4} \times 3{,}210 = 849 \text{ Cal}$$

$$\frac{849}{1{,}918} = 44 \text{ per cent} \quad (4).$$

Water Gas.—In ordinary producer practice the air and the steam are blown in at the same time. If the operation is conducted in cycles, first by blowing in air without steam and then steam without air, the composition of the gas produced is correspondingly altered in cycles. The product of the first stage may be called "air gas." During this stage the temperature of the producer and the fuel bed within it rises rapidly. The gas produced is of low heating value, containing much nitrogen and little hydrogen. It may be discarded entirely, in which case the stage is shortened and the air gas made still poorer by feeding air in larger volume so as to burn a large part of the carbon to CO_2. When the producer has become as hot as safety permits, having thus stored a considerable quantity of heat, the air is shut off and steam introduced. The temperature begins falling and rich "water gas" is produced, very low in nitrogen, consisting essentially of equal volumes of carbon monoxide and hydrogen, only modified by volatile matter, undecomposed steam, and minor irregularities. This continues until the temperature has fallen to the point where the reaction $C + 2H_2O = CO_2 + 2H_2$ begins to take place to an undesirable degree, when the air cycle is begun again. The steam cycle lasts several times as long as the air cycle.

Superheated steam is commonly used in gas producers. The sensible heat thus added to the producer increases the total heat available and makes possible the use of a larger amount of steam.

Example 7

In a water-gas producer 35 per cent of the fuel was consumed during the air cycle and 65 per cent during the steam cycle. The fuel was coke, of the approximate composition 90 per cent carbon and 10 per cent ash. Neglect loss of carbon in the

ashes. During the air cycle, one-half of the carbon burns to CO_2 and one-half to CO; during the steam cycle, assume that all the carbon goes to CO. Only four-fifths of the steam injected is decomposed. Assume that the air is dry.

Required: 1. The relative volumes of air gas and water gas produced.

2. The calorific power (per cubic meter) of the air gas and of the water gas.

3. The percentage of the calorific power of the coke available in the air gas and in the water gas.

4. The volume of air and the weight of steam used for the consumption of 10 tons of coke.

Solution:

$0.35 \times 0.90 = 0.315$ kg. of C burned by air.

$0.65 \times 0.90 = 0.585$ kg. of C burned by steam.

$$\begin{aligned} 2C + O_2 &= 2CO \\ \underline{2C + 2O_2} &\, \underline{= 2CO_2} \\ 4C + 3O_2 &= 2CO + 2CO_2 \text{ (air equation)} \\ C + H_2O &= CO + H_2 \quad \text{(steam equation).} \end{aligned}$$

$0.315 \times \frac{3 \times 22.4}{4 \times 12} = 0.441$ cu. m. of O_2 used in air, producing $\frac{2}{3} \times 0.441 = 0.294$ cu. m. of CO and 0.294 cu. m. of CO_2. Accompanying $N_2 = {}^{79}\!/_{21} \times 0.441 = 1.659$ cu. m. Total volume of air gas $= 0.294 + 0.294 + 1.659 = 2.247$ cu. m.

$0.585 \times \frac{22.4}{12} = 1.092$ cu. m. of CO in water gas; also, 1.092 cu. m. of H_2. $1.092 \times \frac{1}{4} = 0.273$ cu. m. of undecomposed steam.

Total volume of water gas $= 1.092 + 1.092 + 0.273 = 2.457$ cu. m.

Ratio of water gas to air gas $= \frac{2.457}{2.247}$, or 1.09:1 (1).

Calorific power of air gas $= \frac{0.294 \times 3{,}034}{2.247} = 397$ Cal. per cubic meter (2).

Calorific power of water gas $= \frac{1.092\,(3{,}034 + 2{,}582)}{2.457} = 2{,}496$ Cal. per cubic meter (2).

Heating value of the coke $= 0.90 \times 8{,}100 = 7{,}290$ Cal.

Percentage of this in air gas $= \frac{892}{7{,}290} = 12.2$ per cent (3).

Percentage in water gas $= \frac{5{,}616}{7{,}290} = 77.1$ per cent (3).

Volume of air $= (0.441\ O_2 + 1.659\ N_2)\ 10{,}000 = 21{,}000$ cu. m. (4).

Weight of steam $= 1.092 \times \frac{5}{4} \times \frac{18}{22.4} \times 10{,}000 = 11{,}000$ kg. (4).

Problems

64. Coal of the composition given below is made into coke the composition of which follows:

Coal,	Per Cent	Coke,	Per Cent
C	76.3	C	90.8
H	5.4	H	0.4
O	8.8	O	0.9
N	1.8	S	1.0
S	1.2	Ash	6.9
H_2O	1.9		
Ash	4.6		

Required: 1. The weight of coke yielded per ton of coal.

2. The low calorific power of each.

3. The percentage of the heating value of the original coal that can be obtained on burning the coke.

4. Calculate the volume of the products of combustion if the coke is burned with 60 per cent excess air, the air being at 27°C., 765 mm., and 60 per cent humidity.

65. The following coal is used for making coke:

	Per Cent
C	80
H	6
O	8
N	1
Ash	5

The coke is 92 per cent C, 8 ash. The coke-oven gas analyzes:

	Per Cent		Per Cent
C_2H_4	4	CO_2	4
CH_4	35	H_2	44
CO	8	N_2	5

(All dry analyses.) Tar may be neglected.

Required: 1. The kilograms of coke and the cubic meters of gas (dry) made from 1 metric ton of coal.

2 How many cubic meters of air would be required theoretically to burn 1 cu. m. of this gas?

66. A by-product coke plant makes coke analyzing

	Per Cent
C	88.2
H	0.2
Ash	11.6

The coal used is of the following composition:

	Per Cent		Per Cent
C	75.2	N	3.5
H	3.5	H_2O	4.6
O	5.8	Ash	7.4

The coke-oven gas analyzed (dry):

	Per Cent		Per Cent
H_2	56.4	CO_2	1.7
CH_4	28.2	CO	6.1
C_2H_4	2.2	O_2	0.5
C_6H_6	0.8	N_2	4.1

The tar obtained per ton of coal carries 107 lb. of C, and other products 4 lb. of C.

Required: 1. The pounds of coke made from 2,000 lb. of coal.

2. The cubic feet of the coke-oven gas (dry) from 1 ton of coal.

3. The percentage of the original heating value of the coal that is available in the coke.

4. The percentage available in the gas.

67. A by-product coke oven uses coal and produces coke the compositions of which follow:

	Coal, Per Cent		Coke, Per Cent
C	76.5	C	91.7
H	6.8	H	0.2
O	6.4	Ash	8.1
N	1.8		
H_2O	3.0		
Ash	5.5		

The gas issuing from the retorts, analyzed dry, has the following composition:

	Per Cent		Per Cent
CH_4	29.0	H_2	55.4
C_2H_4	3.5	N_2	4.2
CO_2	1.4	NH_3	1.4
CO	5.1		

The temperature of the gas issuing from the retorts is 1000°C.

Required: 1. The kilograms of coal required to make 1 metric ton of coke, and the cubic meters of dry gas issuing from the retorts per metric ton of coke made.

2. When the coke is burned, what percentage of the heating value of the original coal is obtained?

3. *a.* What percentage of the original heating value of the coal is represented by the heating value of the gas?

b. What is the sensible heat content of the gas as it issues from the retort?

68. The following data were obtained from the operation of the by-product coke plant of the Lackawanna Steel Company:

Coal used, per cent		Coke made, per cent		Gas made (dry analysis), per cent	
C	76.8	C	91.7	CH_4	28.5
H	3.5	H	0.2	C_2H_4	2.2
O	6.5	Ash	8.1	C_6H_6	0.7
N	1.7			CO_2	1.4
H_2O	5.7			CO	5.1
Ash	5.8			H_2	56.0
				O_2	0.5
				N_2	4.2
				NH_3	1.4

Per ton of coal, 62.2 kg. of tar was made, carrying 77.7 per cent C and 16.1 per cent H.

Required: Per ton of coal charged:

1. The weight of coke made.

2. The volume of gas made, dry and wet.

3. The percentage of the original calorific power of the coal that is present in the coke.

4. The same for the coke-oven gas.

5. How many kilograms of benzol (C_6H_6) and of ammonium sulphate [$(NH_4)_2SO_4$] will be recoverable?

69. Coal of the following composition is treated in a by-product coke oven:

	Per Cent
C	78
H	5
O	9
N	1.5
Ash	6.5

The coke made analyzes as follows:

	Per Cent
C	89.5
H	1
Ash	9.5

The coke-oven gas analyzes as follows:

	Per Cent		Per Cent
C_6H_6	0.8	CO_2	3.3
C_2H_4	3.0	H_2	44.3
CH_4	34.0	N_2	7.2
CO	6.0	NH_3	1.4

In addition, tar amounting to 3.4 per cent of the coal and containing 90 per cent C is recovered.

Required: 1. The pounds of coal required to make 1 long ton of coke, and the cubic feet of gas yielded therefrom.

2. The pounds of benzol and of ammonium sulphate recoverable per long ton of coal.

3. The calorific powers of the coal, the coke, and the gas.

4. The percentages of the original heating value of the coal that are available in the coke and in the gas.

70. Coal being coked in a by-product plant has the following composition:

	Per Cent
C	77
H	5
O	8
H_2O	3
Ash	7

The coke made has the following composition:

	Per Cent
C	89
H	1
Ash	10

The coke-oven gas as it comes from the retorts consists of the following:

	Per Cent		Per Cent
H_2	50.0	N_2	1.4
CH_4	28.0	CO_2	2.0
CO	8.0	H_2O	6.6
C_2H_4	4.0		

Required: 1. The weight of coke and the volume of gas made, per kilogram of coal.

2. When the coke is burned, what percentage of the original heating value of the coal is obtained?

3. When the gas is burned, what percentage of the heat in the coal is obtained?

4. What temperature will be obtained from burning the coke under theoretical conditions?

5. What temperature will be obtained from burning the gas under theoretical conditions?

71. The following are data on a by-product coke oven operating on coal from Cape Breton, Nova Scotia.

Coal, per cent		Coke, per cent		Tar, per cent		Gas, per cent	
C	76.6	C	87.1	C	89.0	C_6H_6	0.8
H	5.1	H	1.1	H	5.0	C_2H_4	3.0
O	7.2	O	1.9	N	1.0	CH_4	34.0
N	2.5	N	0.7			CO	9.0
S	2.8	S	1.0			CO_2	6.0
Ash	5.8	Ash	8.2			H_2	38.5
						N_2	7.4
						O_2	1.3

The tar yield amounts to 3.38 per cent of the coal used. 20 per cent of the nitrogen of the coal is recovered as ammonia.

Required: 1. The pounds of coke made, per short ton of coal.

2. The cubic feet of gas made, per ton of coal.

3. The percentage distribution of the carbon and hydrogen of the coal in the coke, tar, and gas.

4. The leakage of air into the gas, per ton of coal.

5. How many pounds of benzol and of $(NH_4)_2SO_4$ can be obtained from the gas, per ton of coal?

72. Pocahontas coal from West Virginia was used in a beehive coke oven.

Coal used, per cent		Coke made, per cent		Waste gases made (dried), per cent	
C	84.7	C	89.3	CO_2	14.0
H	4.1	H	0.2	CO	6.4
O	3.6	O	0.2	CH_4	2.4
N	1.0	N	0.3	H_2	3.7
S	0.7	S	0.7	N_2	68.7
H_2O	1.0	H_2O	0.6	H_2O	4.8
Ash	4.9	Ash	8.7		

Required: 1. The kilograms of coke made, per ton of coal.

2. The cubic meters of gases made, per ton of coal.

3. The cubic meters of air used, per ton of coal. (Use both nitrogen and oxygen methods.)

4. What percentage of the original calorific power of the coal is present in the coke?

5. The same for the gases.

6. The percentage distribution of the carbon and of the hydrogen between the coke and the waste gases.

73. A gas producer uses coal of the following composition:

	Per Cent
C	76
H	3
O	6
H_2O	3
Ash	12

It is fed with a mixture of air and steam. The gas made has the following composition:

	Per Cent		Per Cent
CO	24	H_2	14
CH_4	3	N_2	48
C_2H_4	1	H_2O	6
CO_2	4		

The ashes from the producer are one-third carbon.

Required: 1. The cubic meters of gas produced, per kilogram of coal

2. The cubic meters of air supplied, per kilogram of coal.

3. The kilograms of steam fed, per cubic meter of air.

4. The percentage of the original calorific power of the coal that is available in the gas.

74. Coal of the following composition is used in a gas producer:

	Per Cent		Per Cent
C	77.7	N	1.9
H	5.4	H_2O	1.8
O	8.7	Ash	4.5

The ashes from the producer are 25 per cent unburned carbon. The gas made has the following composition:

	Per Cent		Per Cent
CO	22.7	CO_2	5.2
H_2	9.6	N_2	57.4
CH_4	2.4	H_2O	1.9
C_2H_4	0.8		

Required: 1. The cubic feet of gas made, per pound of coal.

2. The cubic feet of air used, per pound of coal (assumed dry).

3. The pounds of steam used, per pound of coal.

4. The percentage of the original calorific power of the coal that is available in the gas.

75. The following data were obtained in the operation of a gas producer:

	Coal Used, Per Cent		Gas Made, Per Cent
C	75	CO	26
H	4	CO_2	3
O	6	CH_4	2
H_2O	5	N_2	50
Ash	9	H_2	15
N	1	H_2O	4

The ashes analyze 25 per cent carbon.

Required: Per kilogram of coal used:

1. The cubic meters of gas made.
2. The cubic meters of air used.
3. The kilograms of steam supplied to the producer.
4. The percentage of the total steam supplied that is decomposed in the producer.

76. A coal analysis was as follows:

	Per Cent
C	84
H	4
O	8
Ash	4

When the coal was used in a gas producer, it gave a gas analyzing:

	Per Cent		Per Cent
CO_2	8	H_2	12
CO	20	N_2	54
CH_4	2	H_2O	4

The ashes amounted to 7 per cent of the weight of the coal. Assume all steam used to be decomposed.

Required: 1. The cubic feet of gas produced, per pound of coal.

2. The cubic feet of air used, per pound of coal.

3 The pounds of steam used, per pound of coal.

4. The heat absorbed in the producer by the steam, per pound of coal.

77. Some of the coal of Prob. 71 is used in a gas producer, making a gas of the following composition:

	Per Cent		Per Cent
CO	24	H_2	15
CO_2	6	H_2O	7
CH_4	2	N_2	46

The ashes from the producer are 15 per cent carbon.

Required: 1. The cubic feet of gas produced, per pound of coal.

2. The calorific power of the coal, per pound.

3. The calorific power of the coke of Prob. 71, per pound.

4. The percentage of the original heating value of the coal which is available in the coke made.

5. Compare the calorific power of the coke-oven gas with that of the producer gas, each per cubic foot.

6. Compare the total heat available in the coke-oven gas with that available in the producer gas, each expressed in percentage of the calorific power of the coal from which made.

78. An open-hearth furnace is fired with gas made from the following coal:

	Per Cent
C	77
H	5
O	8
H_2O	3
Ash	7

At first the gas was made in a gas producer and was of the following composition:

	Per Cent		Per Cent
CO	19.6	H_2	12.8
CO_2	7.8	N_2	55.3
CH_4	2.0	H_2O	2.5

The ashes from the producer amounted to 10 per cent of the coal.

Later the coal was distilled in by-product coke ovens, yielding gas of the following composition (as it comes from the ovens):

	Per Cent		Per Cent
H_2	50	N_2	1.4
CH_4	28	CO_2	2.0
CO	8	H_2O	6.6
C_2H_4	4.0		

The coke from these ovens contained C, 89 per cent; H_2O, 1, ash, 10.

Required: 1. The kilograms of coke made, per 1,000 kg. of coal.

2. In each case, the cubic meters of gas made, per 1,000 kg. of coal.

3. In the producer, the cubic meters of air used, per kilogram of coal.

4. In each case, the calorific power of the gas, per cubic meter.

5. In each case, the percentage of the calorific power of the coal that is available in the gas.

6. The percentage of the calorific power of the coal that is available in the coke.

7. The kilograms of steam fed to the producer, per kilogram of coal, and the percentage of the steam decomposed in the producer.

79. Coal used in a gas producer analyzes as follows:

	Per Cent		Per Cent
C	79.0	N	1.7
H	5.1	H_2O	1.8
O	6.4	Ash	6.0

The gas has the following composition:

	Per Cent		Per Cent
CO_2	7.0	H_2	14.0
CO	21.0	N_2	53.0
CH_4	2.5	H_2O	2.5

The ashes amount to 9 per cent of the coal. The air used is 80 per cent saturated with H_2O vapor. Temperature, 26°C., barometer, 740 mm.

Required: 1. The volume of gas made, per kilogram of coal.

2. The volume of air (moist) at standard conditions used, per kilogram of coal.

3. The weight of steam used, per kilogram of coal.

4. The percentage of the H_2O blown in that was decomposed in the producer.

5. The percentage of the original calorific power of the coal that is available in the gas.

80. A gas producer uses coal that analyzes (dry) as follows:

	Per Cent
C	75.68
H	4.50
O	12.70
Ash	7.12

As used, the coal carries moisture equal to 3.4 per cent of the dry coal. The ashes from the producer contain 21.07 per cent unburned carbon.

The gas produced analyzes (dry) as follows:

	Per Cent		Per Cent
CO	5.7	H_2	10.5
CO_2	22.0	O_2	0.4
CH_4	2.6	N_2	58.2
C_2H_4	0.6		

In addition, the gas carries 30.4 g. of moisture to each cubic meter of dry gas.

Both air and steam are supplied to the producer by a blower. In addition to the steam, the air carries 15 g. of water vapor per cubic meter of dry air, owing to humidity.

Required: 1. The volume of dry gas produced, per kilogram of dry coal.

2. The weight and volume of air supplied, per kilogram of dry coal, measuring the air in its moist condition and at 20°C.

3. The weight of steam supplied, per kilogram of dry coal.

4. The percentage of the steam supplied that is not decomposed in the producer.

81. The compositions of the coal used and of the gas made in a gas producer are given below:

	Coal, Per Cent		Gas (Dry), Per Cent
C	76.2	CO_2	5.9
H	5.0	CO	22.6
O	10.6	CH_4	2.7
N	1.4	C_2H_4	0.4
H_2O	1.1	H_2	12.6
Ash	5.7	N_2	55.8

The ashes produced carried 15.1 per cent unburned carbon. There was removed from the gas 13 grains of water vapor per cubic foot of dried gas. The air used carried 2.2 per cent water vapor.

Required: 1. The analysis of the wet gas

2 The cubic feet of wet gas made, per pound of coal.

3. The cubic feet of air used (moist).

4. The pounds of steam used.

5. The percentage of the steam injected that was decomposed in the producer, assuming moisture in the air to have been decomposed in the same percentage as the steam.

82. The following coal is used in an air-gas producer, making 4 cu. m. of a gas of the given composition per kilogram of coal. The gases leave the producer at a temperature of 750°C.

	Coal, Per Cent		Gas, Per Cent
C	75.0	CO	27
H	3.6	CO_2	3
O	6.4	CH_4	2
H_2O	6.0	H_2	6
Ash	9.0	N_2	62

Required: 1. The percentage of the calorific power of the coal in:

a. The unburned carbon in the ashes.

b. The calorific power of the gas.

c. The sensible heat in the gas.

d. The heat lost by radiation and conduction.

2. If steam is used to reduce the heat losses, how much steam would be required to reduce the heat lost in the gases by one-quarter and the radiation and conduction losses by one-third? (Neglect sensible heat in the steam.)

3. Assuming all other reactions to remain the same, what would be the composition of the new gas?

4. What percentage of the original calorific power of the coal will be present in the new gas?

83. A Dellwick-Fleischer water-gas producer uses the following coal:

	Per Cent
C	64.0
O	10.9
H	4.7
H_2O	8.6
Ash	11.8

The producer is operated by feeding it alternately with air alone and with steam alone, thus producing alternately pure air gas and pure water gas. 28 per cent of the coal fed is burned during the air cycle and 72 per cent during the steam cycle. Neglect carbon in the ashes.

The gases analyze:

	Air Gas, Per Cent
CO	9.7
CO_2	33.1
CH_4	1.5
H_2	16.6
N_2	35.0
H_2O	4.1

	Water Gas, Per Cent
CO	36.5
CO_2	1.0
CH_4	2.7
H_2	47.0
H_2O	12.8

Assume that in both cycles the oxygen of the coal combines with carbon, the hydrogen remaining free.

Required: 1. Per kilogram of total coal used, the cubic meters of (*a*) air gas, and (*b*) water gas produced.

2. The calorific power of each of these gases per cubic meter, and the percentage of the original calorific power of the coal found in the total volume of each.

3. The kilograms of steam fed during the steam cycle, per kilogram of total coal burned during both cycles.

4. The percentage of the steam fed that is decomposed in the producer.

5. *a*. The heat generated by the combustion of the carbon to CO and CO_2 during the air cycle.

b. The excess heat absorbed by the decomposition of steam over that generated by the combustion of carbon during the steam cycle, each expressed per kilogram of total coal burned during both cycles.

84. A water-gas producer uses coke as fuel, containing 90 per cent fixed carbon and 10 per cent ash.

When on steam, the temperature of the fuel bed runs an average of 1000°C., and the gas produced contains (dried):

	Per Cent
H_2	50.7
CO	48.0
CO_2	1.3

Tests showed that 94 per cent of the steam used had been decomposed. When running on air (dry), the gases produced were CO_2, 21.0 per cent; N_2, 79.0.

2.40 cu. m. of actual (moist) water gas is produced, per kilogram of coke charged Temperature of hot water gas and hot combustion gases leaving fuel bed, 1000°C.

Required: 1. What percentage of the coke is burned by steam, and what by air? (Calculate on the basis of 1 kg. of coke used.)

2. What percentage of the calorific power of the coke is represented by the potential calorific power of the water gas formed?

3. What proportion of the calorific power of the coke is carried off as sensible heat by the hot gases during each period (on steam and on air)?

85. A water-gas producer uses coal containing 90 per cent carbon and 10 per cent ash. The producer is fed with air alone for 7.5 min. and then with steam alone for 4 min., carbon being consumed at the same rate per minute during each of these cycles. 2 per cent of the carbon is lost in the ashes. The air cycle burns the carbon half to CO and half to CO_2, and the steam cycle burns it entirely to CO. Only four-fifths of the steam blown in is decomposed

Required: 1 The volume of water gas made, per cubic meter of air gas made

2. The calorific power, per cubic meter, of the air gas and of the water gas

3. The percentage of the original calorific power of the coal that is available in the air gas and in the water gas

4 The cubic meters of air used, per kilogram of steam; and the cubic meters of air and the kilograms of steam used, per kilogram of coal.

86. A coal contains:

	Per Cent
Volatile matter	25
Fixed carbon	60
H_2O	3
Ash	12

The calorific power of the volatile matter is 9,250 Cal per kilogram (low c.p)

The calorific power of the fixed carbon is 8,100 Cal per kilogram

The coal is used in a gas producer in which the volatile matter is first distilled into the gas without combustion. The composition of the producer gas is the volatile matter + H_2O of coal + gas from combustion of the fixed carbon (assumed to burn to CO).

Required. 1. What volume of dry air is required per kilogram of coal used?

2. If no H_2O is in the air required to run the producer, what is the calorific power of the gas in percentage of the calorific power of the coal?

3. How much steam (in kilograms), per kilogram of coal used, will be necessary to absorb one-half the heat generated in the producer, neglecting sensible heat in the steam?

4. What will be the calorific power of the gas in percentage of the calorific power of the coal when this steam is used?

87. Bituminous coal used in a gas producer contains:

	Per Cent
Moisture	1
Volatile matter	21
Fixed carbon	70
Ash	8

	Per Cent
C	78
H	5
O	8
Ash	8
Moisture	1

The gas formed without using steam contains (dried):

	Per Cent
CO	35
CO_2	5
CH_4	5
H_2	5
N_2	50

The gas leaves the producer at 500°C The calorific power of the coal (practical) is 7,480 Cal.

Required· 1. The volume of gas obtained, per kilogram of coal.

2. The calorific power of the gas produced, per cubic meter

3. What proportion of requirement 2 is due to the volatile matter of the coal, and what proportion to real producer gas?

4. Make a heat balance of the producer, to account for the calorific power of the coal.

5. How much greater would the calorific power of the gas from 1 kg. of coal become if 0 3 kg of steam were used per kilogram of coal, assuming all of it decomposed in the producer?

6. What would be the composition of the gas produced in requirement 5?

88. A bituminous coal contains

	Per Cent
C	78
H	5
O	8
Ash	9

When used in a smaller gas producer without steam, it produced the following gas (dry analysis).

	Per Cent
CO	35
CO_2	5
CH_4	5
H_2	5
N_2	50

The ashes amounted to 13 per cent of the coal. The gas left the producer at 500°C.

The coal was then used in a larger producer, and enough steam was blown in to reduce the heat lost as sensible heat in the hot gas by one-fourth and the radiation, convection, and conduction loss by one-third. Assume that the volume of CO_2 and of CH_4 and the amount of ashes made in this producer were the same as in the smaller one

Required: 1. The volume of gas (dry) produced, per kilogram of coal, in the smaller producer.

2. The calorific power of this gas, and the percentage of the calorific power of the coal available in the gas.

3. The number of calories lost in this producer, per kilogram of coal:

a Through unburned carbon in ashes.

b. As sensible heat in the gas

c. By combined radiation, convection, and conduction (by difference)

4. The kilograms of steam blown in, per kilogram of coal, in the larger producer (assume steam all decomposed, and neglect its sensible-heat content).

5. The percentage composition of the gas made in this producer.

6. The calorific power of this gas, per cubic meter, and the percentage of the calorific power of the coal available in it.

89. A gas producer uses the following coal:

	Per Cent
C	77.5
H	3.0
O	6.0
H_2O	3.5
Ash	10.0

The ashes from the producer are 20 per cent unburned carbon.

The producer is fed with a mixture of air and steam, four-fifths of the carbon burned being burned by air and one-fifth by steam. Only 80 per cent of the steam blown in is decomposed. Of the carbon burned by air, one-third goes to CO_2, the balance to CO, while all the carbon burned by steam goes to CO.

The oxygen of the coal combines with carbon; assume that all the hydrogen of the coal remains uncombined.

Required: 1. The cubic meters of producer gas made, per kilogram of coal.

2. The percentage of the heat generated by burning of carbon in the producer that is absorbed by decomposition of the steam.

90. Coke of the composition C, 76 per cent; H_2O, 6 per cent; ash, 18 per cent is used in a gas producer making mixed gas. The amount of steam is 1 kg. to 8 cu. m. of air, but only 75 per cent of this steam is decomposed. Assume no hydrocarbons in the gas, and neglect the carbon in the ashes.

Of the carbon burned by air, three-fourths goes to CO and one-fourth to CO_2. All carbon burned by steam goes to CO.

Required: 1. The percentages of the carbon burned by the air and by the steam.

2. The volume and percentage composition of the gas, per kilogram of coke.

91. The gas producers of the New Jersey Zinc Company at Palmerton, Pa., burn anthracite coal, the composition of which is approximately as follows:

	Per Cent
C	88
H_2O	3
Ash	9

The producers are fed with a mixture of air and steam containing one-seventh steam by volume. 90 per cent of the steam is decomposed in the producer, forming CO and hydrogen. The air forms CO and CO_2 in the proportion of 4:1. The ashes from the producer contain 12 per cent unburned carbon.

Required: 1. The volume of gas produced, per kilogram of coal, and its percentage composition.

2. The amount of heat saved by using the steam, and the proportion of the calorific power of the gas represented by this amount.

92. The following coal was used in a gas producer:

	Per Cent		Per Cent
C	75	S	3
H	4	H_2O	5
O	6	Ash	7

The ashes weigh 10 per cent of the coal. There was used, per kilogram of coal, 3.1 cu. m. of air, assumed dry. Of the carbon going into the producer gas, two-thirds is present as CO, one-fourth as CO_2, and one-twelfth as CH_4.

Assume that all the CO_2 in the gas results from the air reaction, none being formed in the steam reaction. Hydrogen in the coal is not oxidized; oxygen in the coal forms CO and CO_2. Part of the air is used in burning all the sulphur to SO_2

Required: 1. The kilograms of steam used, per kilogram of coal.

2. The cubic meters of gas produced, per kilogram of coal.

3. The percentage of the calorific power of the coal that is available in the gas.

93. A gas producer uses coal containing the following:

	Per Cent
C	75
H	4
O	6
H_2O	6
Ash	9

It is supplied with air and steam in the ratio of 7 cu. m. of air to 1 kg. of steam. Assume the moisture of the coal evaporated and appearing as water vapor in the gas produced, 80 per cent of the steam supplied is decomposed, and 20 per cent goes into the gas as water vapor; 90 per cent of the carbon that is burned by air goes to CO, and 10 per cent to CO_2. Assume the oxygen of the coal to burn carbon, forming CO and CO_2 in the same ratio as oxygen from the air. All the carbon burned by steam goes to CO. 5 per cent of the carbon of the coal goes over to the gas as CH_4, and 2 per cent is lost in the ashes.

Required: 1. The cubic meters of gas made, per kilogram of coal.

2. The percentage composition of the gas as made.

3. The percentage of the total carbon that is burned by air and by steam.

4. The percentage of the calorific power of the coal that is present in the gas.

94. A gas producer is fed with a mixture of 1.2 kg. of steam to 10 kg. of air. Only five-sixths of the steam is decomposed. Of the carbon burned by air, one-fourth goes to CO_2; all the carbon burned by steam goes to CO. From each kilogram of coal the following is distilled off in the top of the producer:

	Kilograms		Kilograms
CH_4	0.07	H	0.02
C_2H_4	0.06	CO	0.03
C_6H_6	0.04	H_2O	0.03

The remainder of the coal contains 0.65 kg. of carbon and 0.10 kg. of ash. The ashes from the producer contain 25 per cent unburned carbon.

Required: 1. The percentage of the fixed carbon of the coal that is:

- *a.* Lost in ashes.
- *b.* Burned by air.
- *c.* Burned by steam.

2. The volume of gas produced, per kilogram of coal.

3. The percentage composition of the gas by volume.

4. The amount of heat saved by using steam, per kilogram of coal used.

95. A Mond gas producer is fed with a mixture of air and steam, using 2.5 kg. of steam for every kilogram of coal consumed.

The composition of the coal is as follows:

	Per Cent		Per Cent
C	62.7	N	1.4
O	10.9	H_2O	8.6
H	4.6	Ash	11.8

The ashes amount to 15.5 per cent of the coal. Assume all the nitrogen of the coal to appear in the gas as NH_3. 5 per cent of the carbon in the coal goes into the gas as CH_4. Assume all the oxygen in the coal to combine with carbon, one-half the carbon going to CO and one-half to CO_2. All the carbon burned by air and by steam also goes one-half to CO and one-half to CO_2. Of the steam blown in, only 20 per cent is decomposed.

Required: 1. The volume of air used, per kilogram of coal.

2. The volume of gas produced, per kilogram of coal

3. The percentage of the original calorific power of the coal that is available in the gas produced (excluding NH_3).

CHAPTER V

THERMOCHEMISTRY AND THERMOPHYSICS

THERMOCHEMISTRY

Chemical changes are in general accompanied by either liberation or absorption of heat. This is evidence of the fact that the total energy content of the system existing before the chemical change is different from the energy content of the system existing after the chemical change. The chemical change is accompanied by a redistribution of energy; and while the action may often be caused to take place in such a manner that liberation or absorption of electrical or some other form of energy accounts for part of the total energy change, in the majority of chemical and metallurgical processes liberation or absorption of heat energy accounts for nearly all of it.[1]

As an example, consider a system composed of 112 kg. of iron and 48 kg. of free oxygen, both at 18°C. This system may be regarded as having a certain total energy content, made up chiefly of latent chemical energy. Now, if the two components of the system are caused to unite chemically, there results a system composed of 160 kg. of the iron oxide Fe_2O_3; and this system, when brought to a temperature of 18°C., will have a total energy content 198,500 Cal. less than the original system:

$$2Fe + 3O = Fe_2O_3 + 198,500 \text{ Cal.}$$

The energy equivalent to 198,500 Cal. has, of course, not been destroyed; it has merely been transferred to the surroundings. Much of it may be retained for a short time as sensible heat by the Fe_2O_3 but is lost as the Fe_2O_3 cools to 18°. If the chemical reaction takes place rapidly, as in roasting iron pyrite, the Fe_2O_3 becomes very hot; but if the reaction takes place slowly, as in rusting of iron, the heat is dissipated to the surroundings as fast as it is generated.

Symbols for Change of Heat Energy and Their Signs.—In thermodynamics it is customary to think in terms of the energy content of the original system; heat evolved in a reaction represents a *decrease* in the energy possessed by the original system (reactants). Therefore, heat evolved is given a negative sign. Change of energy content, represented here by heat evolved or absorbed, is given the symbol ΔH. When heat is evolved (an exothermic reaction), ΔH is a negative quantity; when heat is absorbed (an endothermic reaction), ΔH is a positive quantity.

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[1] The change of heat content in a reacting system (heat of reaction) is thus equal to the decrease of total energy of the system. It is not, however, equal to the decrease of free energy of the system. The significance of free-energy change is discussed in Chap. XXIV.

In thermochemistry the symbol Q has been used for the heat of reaction and has been called positive when heat is evolved and negative when heat is absorbed. For example, an exothermic reaction has been written as follows:

$$C + O_2 = CO_2 + 97{,}200 \text{ Cal.}$$

And an endothermic reaction has been written as follows:

$$CO_2 + C = 2CO - 38{,}880 \text{ Cal.}$$

Thus, in a reaction taking place under the usual conditions of constant pressure:

$$\Delta H = -Q.$$

While the symbol Q and its accompanying sign convention were used in the first edition of this book, the use of the thermodynamic convention has become so much favored in recent years that ΔH and its accompanying sign convention will be adopted in the present edition. The above equations will be written:

$$C + O_2 = CO_2; \qquad \Delta H = -97{,}200 \text{ Cal.}$$

and

$$CO_2 + C = 2CO; \qquad \Delta H = +38{,}880 \text{ Cal.}$$

Heat of Formation of Compounds.—Evidently the formation of Fe_2O_3 from Fe and O liberates heat. The quantity of heat liberated is called the *heat of formation* of Fe_2O_3. Its value is $\Delta H = -198{,}500$ Cal. per molecular weight (in kilograms).[1] Since the molecular weight contains 112 kg. of Fe, the heat of formation of Fe_2O_3 may also be expressed as $\frac{-198{,}500}{112}$ or $-1{,}770$ Cal. per kilogram of Fe and $\frac{-198{,}500}{160}$ or $-1{,}240$ Cal. per kilogram of Fe_2O_3.

Tables XXVI to XLIX, pages 404 to 421, give the heats of formation of various compounds in Calories, given in one column per molecular weight of the compound in kilograms, and in another column per unit weight (kilogram) of the metal or corresponding element. In the tables, for convenience, the values given are those for $-\Delta H$, so that a positive value in the table represents heat generated in formation of the compound. In a few cases the heat of formation is designated as negative, meaning that the heat is absorbed instead of generated when the compound is formed.

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[1] The molecular weight is also called the *formula weight* or the *molal weight*. The heat of formation per molecular weight may be termed the *molal heat of formation*.

The values of heats of formation may be conveniently indicated in connection with the chemical reaction symbolizing the formation, thus:

$$2Fe + 3O = Fe_2O_3; \qquad \Delta H = -198{,}500 \text{ Cal.},$$

it being understood that the quantity of heat shown is the quantity corresponding to the number of molecules of Fe_2O_3 in the equation. If the equation be doubled, for the purpose of expressing the oxygen in number of molecules of O_2, we must write:

$$4Fe + 3O_2 = 2Fe_2O_3; \qquad \Delta H = -397{,}000 \text{ Cal.}$$

An abbreviated manner of indicating the heat of formation, and the one adopted for the tables, is to write $(Fe_2,O_3) = -198{,}500$ Cal., the comma indicating union of the elements enclosed in parentheses. Here it is understood that the quantity of heat is ΔH *per molecular weight* for the formula indicated between the parentheses.

Often the same compound may be formed from different materials. Thus FeS_2 may result from Fe + 2S or from FeS + S. Similarly $CaCO_3$ may be formed from Ca + C + 3O, from Ca + O + CO_2, or from CaO + CO_2. The heats of formation naturally differ but are readily differentiated in the system adopted. We write:

$$\begin{aligned}(Fe,S_2) &= -35{,}500 \text{ Cal.}\\ (FeS,S) &= -12{,}400 \text{ Cal.}\\ (Ca,C,O_3) &= -289{,}500 \text{ Cal.}\\ (Ca,O,CO_2) &= -195{,}050 \text{ Cal.}\\ (CaO,CO_2) &= -43{,}450 \text{ Cal.}\end{aligned}$$

Heat of Decomposition.—Let us now consider the reverse process of decomposition of Fe_2O_3 into its elements 2Fe and 3O. To perform this decomposition will require the absorption of a quantity of energy equal to the amount liberated when Fe_2O_3 is formed. Here 198,500 Cal. will be needed to reduce 160 kg. of Fe_2O_3. This principle may be expressed by the statement that **the heat of decomposition of a compound is equal to its heat of formation but of opposite sign.**

When it is desired in practice to reduce Fe_2O_3, it is not sufficient merely to heat the Fe_2O_3, though relatively weak oxides may be reduced by heating alone. In general merely supplying the heat of decomposition will not cause the decomposition to occur. There must be a suitable reducing agent to combine with the oxygen and remove it, or else the reduction must be performed by electrolysis, supplying the necessary energy in the electrical form. With Fe_2O_3, in practice the cheapest method is to use carbon or CO as a reducing agent:

$$Fe_2O_3 + 3C = 2Fe + 3CO \tag{1}$$

or

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2. \tag{2}$$

Thus the carbon or CO is oxidized, which *liberates* energy and thus supplies part (sometimes all) of the energy needed. An additional amount of carbon burned as fuel liberates additional heat to supply the balance, as well as to produce the necessary operating temperature, melt the iron and the slag, etc. The thermochemical equations of combustion of carbon are:

$$\begin{aligned} C + O &= CO; & \Delta H &= -29{,}160 \text{ Cal.} \\ C + O_2 &= CO_2; & \Delta H &= -97{,}200 \text{ Cal.} \end{aligned}$$

Heat of Reaction.—Evidently reaction (1) above is a combination of the reaction

$$Fe_2O_3 = 2Fe + 3O; \qquad \Delta H = +198{,}500 \text{ Cal.} \tag{3}$$

and the reaction

$$3(C + O) = 3CO; \qquad \Delta H = -3(29{,}160) \text{ Cal.} \tag{4}$$

Adding reactions (3) and (4):

$$Fe_2O_3 + 3C = 2Fe + 3CO; \qquad \Delta H = +111{,}020 \text{ Cal.}$$

It is not necessary, however, to separate into two reactions and then recombine. We may write:

$$\begin{aligned} &Fe_2O_3 + 3C = 2Fe + 3CO \\ \Delta H = {}&+198{,}500 \qquad - 3(29{,}160) = +111{,}020 \text{ Cal.,} \end{aligned}$$

placing the heats of formation or decomposition under the respective compounds with the proper sign and adding algebraically. Similarly Eq. (2) becomes:

$$\begin{aligned} &Fe_2O_3 + 3CO = 2Fe + 3CO_2 \\ \Delta H = {}&+198{,}500 + 3(29{,}160) \qquad - 3(97{,}200) = -5{,}620 \text{ Cal.} \end{aligned}$$

In this manner the heat evolved or absorbed by any chemical reaction, called its *heat of reaction*, may be calculated from the heats of formation of the compounds involved.

By applying the same principle, the heat of formation of a compound may be calculated from the heats of formation of two other compounds from which the compound in question may be derived. For example, there was given on page 81 the heat of formation $(\mathrm{Ca,O,CO_2}) = -195{,}050$ Cal. The heat of formation of $(\mathrm{Ca,O}) = -151{,}600$ Cal. If this second combination takes place between the Ca and O occurring in the first expression, the first expression becomes $(\mathrm{CaO,CO_2})$, and its heat of formation is obtained by subtracting $-151{,}600$ from $-195{,}050$, so that $(\mathrm{CaO,CO_2}) = -43{,}450$ Cal. The equations may make the relation more clear:

$$\mathrm{Ca + O + CO_2 = CaCO_3}, \qquad \Delta H = -195{,}050 \text{ Cal.}$$

$$\mathrm{Ca + O = CaO}; \qquad \Delta H = -151{,}600 \text{ Cal.}$$

Subtracting:

Therefore:

$$\left.\begin{array}{l}\mathrm{CO_2 = CaCO_3 - CaO};\\ \mathrm{CaO + CO_2 = CaCO_3};\end{array}\right\} \qquad \Delta H = -43{,}450 \text{ Cal.}$$

This principle is extremely useful in determining and checking heats of formation and is applied continually by experimenters in thermochemistry. It often permits also the calculation of a heat of formation from an experimental determination of a different heat of reaction.

Heat of Combination.—Heat of formation is often called *heat of combination* when referring to the combining elements rather than to the compound formed. Heat of combination of an element with oxygen may be called *heat of oxidation.*

Heat of Solution.—An energy change also occurs when a compound dissolves in water or other solvent. It may result in either liberation or absorption of heat, causing the temperature of the solution to rise, as with sulphuric acid in water, or to fall, as with potassium cyanide in water. The heat of solution is accordingly either negative or positive.

It follows that the heat of formation of a soluble salt when formed in solution is different from the value when it is formed as an anhydrous compound. The difference between these two values is equal to the heat of solution. The value of the heat of solution varies with the concentration of the solution. In general it is larger (positively or negatively) in dilute solution than in a concentrated solution. After the solution has become fairly dilute, there is little change from further dilution. The tables give, in the case of the more important soluble salts, the heats of formation both for the anhydrous material and "in dilute solution." The latter value is applicable whenever the weight of water is several times the weight of the compound dissolved. It is necessarily indefinite; but heats of solution, while large enough to be important, are small enough so that some degree of indefiniteness or variation from the true value will not cause an appreciable error.

Heat of Dilution.—From the discussion of heat of solution it follows that making a solution more dilute will also liberate or absorb heat. Except when a rather concentrated solution is made dilute, the change is small. Heat of dilution is of little practical importance to the metallurgist and will not be further considered in this book.

Heat of Formation of Alloys.—When two metals form a solid solution, the heat of formation of the alloy is simply the heat of solution of one metal in the other. It is a small figure and may be either positive or negative.

When a chemical compound is formed between the alloying elements, the heat of formation of the compound must also be considered. It may be either small or large; the ΔH is usually negative. Solution of such a compound in the remainder of the alloy, when it occurs, affords further possibility of heat change—one about which, incidentally, there is little or no exact knowledge.

When the metal components exist as separate crystals of pure metal, as in a eutectic, however fine and intimately mixed the crystals may be, there is no heat of formation involved. There is, of course, a heat of solution of the constituents *while molten*, but this is counterbalanced by the same quantity of opposite sign when the alloy solidifies and the metals separate from solution.

Few data are available on heats of formation of alloys, though the question is an important one.

THERMOPHYSICS

Whereas thermochemistry deals with heat in relation to chemical changes, thermophysics has to do with heat as affected by physical changes, with particular reference to change of temperature and change of phase.

If the temperature of a body initially at 0°C. is raised to t°C., provided the body has undergone no change of phase, it will have gained a quantity of heat equal to its weight times its mean specific heat between 0 and t times t. A change of phase, such as is excluded in this statement, may be melting, vaporization, allotropic transformation, sublimation, etc., any of which in general may occur at a definite temperature without temperature change. Such changes involve absorption or liberation of heat. If there is no such change of phase involved, the heat content of a body at t°C. may be taken for practical purposes as the product mentioned. This formulation deliberately, for reasons of convenience, ignores the heat content of the body at 0°C. (A parallel formulation may be made in Fahrenheit units.) The subject of specific heat and sensible-heat content has been discussed on pages 29 and 30.

The *heat capacity* of a body is its weight multiplied by its specific heat. The expression "heat capacity per gram," therefore, often used in tables, has the same meaning as that of specific heat in the ordinary weight unit.[1] The *mean* heat capacity between t_1 and t_2 multiplied by the change in temperature $(t_1 - t_2)$ gives the change in sensible-heat content in going from t_1 to t_2.

If $t°$ is above the melting point of the body, then the relation just discussed may be applied only up to the melting point. Here the body changes to the liquid phase and in so doing receives or takes up an additional quantity of heat called the *latent heat of fusion.* After melting, the above relation may again be applied up to the boiling point, but now with a different specific heat, *viz.*, that of the liquid, applied to the rise in temperature above the melting point. At the boiling point an additional quantity is again absorbed, the *latent heat of vaporization.* Above the boiling point the specific heat of the vapor must be used. When the body cools, the same changes take place in the reverse direction, the latent heats of change being liberated instead of absorbed.

Some substances undergo transformations other than those of fusion and vaporization, such as the well-known allotropic changes of sulphur and the critical changes of iron. There is a similar absorption or liberation of heat accompanying each of these, usually a small quantity. For example, the changes from pure α- to γ-iron and from γ- to δ-iron, taking place at about 910 and 1400°C., respectively, absorb about 3.9 and 1.9 Cal. per kilogram, respectively, while the latent heat of fusion of iron is 65 Cal. and the latent heat of vaporization about 1,515 Cal. per kilogram.

Dulong and Petit's Law.—Dulong and Petit long ago observed that the specific heats of elements are related to their atomic weights. They formulated a law which may be stated as follows: **The product of the specific heat of an element times its atomic weight is a constant, substantially the same for all elements.**

Practically it has been found that not only are there some exceptions to this statement but that in general the word "substantially" must be interpreted with liberality. For example, the specific heats increase with temperature, though slowly—in many cases about 4 per cent for each 100°C. Also, even at 0° (or any other temperature), the product is only roughly constant for different substances. For solid metals the value at 0°C. varies between 6 and 7, averaging about 6.4.

From Dulong and Petit's law it follows that elements having high atomic weights have low specific heats, and vice versa. Accurate experimental determinations of the specific heats of elements have rendered the law of theoretical interest only—with one important exception. It has been found that in the case of monatomic vapors the constant noted above is indeed practically a constant and has the value of 5.0. Since most metals in the vapor state are always monatomic, this relation enables one to determine easily the specific heat of a metal vapor, a quantity which can be measured experimentally only with great difficulty and in many cases not at all. The specific heat of a metal vapor, then, is 5.0 cal. per gram-atom, or $\frac{5.0}{22.4} = 0.223$ Cal. per cubic meter. These statements refer to the specific heat at constant pressure, c_p.

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[1] Although it seems preferable to differentiate between "heat capacity" and "specific heat" as here indicated, in many books the term "heat capacity" is always used with reference to one unit of the substance and thus has the same meaning as "specific heat."

This value apparently does not vary appreciably with temperature. It has been used in calculations for various metal vapors frequently and with considerable confidence.

Summary.—Let it be required as an example to calculate the heat content of 1 kg. of nickel (vapor) at 3500°C. Nickel undergoes a transformation in the solid state (α- to β-nickel) at about 352°C. It melts at 1455°C. and boils at about 2730°C. In going from α- to β-nickel, 1 kg. absorbs 1.33 Cal. The latent heat of fusion of nickel is 72 Cal. per kilogram. The latent heat of vaporization has not been determined directly, but a method of calculation gives 1,490 Cal. as an approximation. The mean specific heat of solid nickel between 0 and 200°C. has been determined as $0.1032 + 0.000051t$. In the absence of other data, this expression may be assumed to apply up to the transformation point. The specific heat of β-nickel is 0.128 at 360°C. and remains approximately constant up to the melting point The specific heat of molten nickel is known to be slightly greater than that of solid nickel. Its exact value is uncertain since different published results are at variance. The most recent determination is 0.16. The specific heat of the vapor is probably close to 5.0 Cal. per molecular weight of 58.7 kg From these values, the specific heat of nickel vapor per kilogram is calculated as 0.085.

With the above constants, the calculation now proceeds as follows:

Heat in 1 kg. of α-nickel at 352° = $(0.1032 + 0.000051 \times 352)352$	=	42.6	Cal.
Latent heat of transformation, α to β	=	1.3	
Heat in 1 kg. of β-nickel at 352°	=	43.9	Cal.
Heat gained between 352 and 1455° = $0.13 \times (1{,}455 - 352)$	=	143	
Heat in 1 kg of solid nickel at the melting point (1455°)	=	187	Cal.
Latent heat of fusion	=	72	
Heat in 1 kg. of liquid nickel at the melting point	=	259	Cal
Heat gained between 1455 and 2730° = $0.16 \times (2{,}730 - 1{,}455)$	=	204	
Heat in 1 kg. of liquid nickel at the boiling point (2730°)	=	463	Cal
Latent heat of vaporization	=	1,490	
Heat in 1 kg. of nickel vapor at the boiling point	=	1,953	Cal.
Heat gained between 2730 and 3500° = $0.085 \times (3{,}500 - 2{,}730)$	=	65	
Heat in 1 kg. of nickel vapor at 3500°	=	2,018	Cal

The labor of determining the above quantity would be greatly lessened if some of the intermediate quantities were known. For example, if the heat content of liquid nickel at the boiling point (463 Cal.) were given, only two short steps would be necessary to arrive at the result. Similarly, if the heat content of liquid nickel at the melting point (259 Cal.) be given, one short step will give the heat content of the liquid at a desired temperature. Table XIV, page 391, gives values of heat contents for different metals at their melting points and at their boiling points.

The heat content of 1 kg. of the solid metal at the melting point may be designated q_M, and that of the liquid metal at the boiling point is designated q_B. It is important to consider the precision of these quantities. The values of q_M for the common metals are known with a satisfactory degree of precision. The values of q_B are less well determined, but in most cases the probable error does not exceed ±5 to 10 per cent. The values of all heat contents above q_B, however, are more uncertain, owing especially to the uncertainty in the value of the latent heat of vaporization, which, as appears above in the case of nickel, is always so large a quantity as to outweigh all the other quantities.

Expressions for Heat Content and Specific Heat and the Use of Tables.—The sensible heat content above 0°C. of a body at temperature t may be expressed in general terms as follows, when no change of phase takes place in the body while its temperature changes from 0 to t:

$$q = W \times c_m \times t, \tag{5}$$

where W is the weight of the body in grams or kilograms and c_m is the mean specific heat (per gram or per kilogram) between 0 and $t°$. This expression has already been given on page 30; it follows directly from the definition of specific heat. The heat content of 1 g. of the substance is given by:

$$q = c_m t.$$

That of 1 mol is given by:

$$Q = C_m t.$$

The heat capacity of a body is equal to $W \times c$, or $W \dfrac{dq}{dt}$ and the molal heat capacity of a substance is equal to C, or $\dfrac{dQ}{dt}$.

It has been found that the specific heat varies with temperature, and c_m may be written empirically in the form $A + Bt + Ct^2 + \cdots$, where A is the specific heat at 0°, and B, C, etc., are other constants for the substance in question. Ct^2 is often negligible in magnitude and Dt^3 and succeeding terms usually so.

At 0°: $q = At$.

At $t°$: $q = (A + Bt + Ct^2)t, \qquad (6)$

where B and C apply *only* to the *mean* specific heat c_m. If these values of B and C are not known, but the values are known of α and β, representing the corresponding constants in the expression for the actual ("instantaneous") specific heat at temperature t, α being the specific heat at 0° ($\alpha = A$), then the actual specific heat at $t°$ is given by:

$$c_t = \alpha + \beta t + \gamma t^2. \tag{7}$$

And the heat content above 0° at $t°$ is given by:

$$\begin{aligned} q &= \int_0^t (\alpha + \beta t + \gamma t^2)\, dt & (8) \\ &= \alpha t + \tfrac{1}{2}\beta t^2 + \tfrac{1}{3}\gamma t^3 \\ &= (\alpha + \tfrac{1}{2}\beta t + \tfrac{1}{3}\gamma t^2)t. & (9) \end{aligned}$$

Equation (9), it will be observed, is applicable for finding the heat content at $t°$, when the expression for the actual specific heat at $t°$ is given instead of the mean specific heat. Equation (8) is a more general form of Eq. (6), and it is obvious that the coefficients in the expression for mean specific heat between 0 and $t°$ are related as follows to the corresponding coefficients in the expression for actual specific heat at $t°$ when the latter is given in the form of Eq. (7): $A = \alpha$, $B = \tfrac{1}{2}\beta$, $C = \tfrac{1}{3}\gamma$.

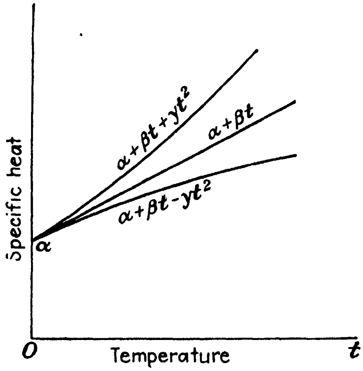

FIG. 3.—Variation of specific heat with temperature (empirical)

When C is negligible, the graph of $c_t = A + Bt$ is a straight line, and the mean value of B is its value halfway between 0 and t, or $\alpha + \tfrac{1}{2}\beta t$; but when C is not negligible, then $c_t = A + Bt + Ct^2$ is a parabolic curve, in which $C = \tfrac{1}{3}\gamma$ (see Fig. 3).

The change in sensible heat when the temperature changes from t_1 to t_2 may be expressed as:

$$dq = \int_{t_1}^{t_2} (\alpha + \beta t + \gamma t^2 + \cdots)\, dt. \tag{10}$$

For many substances, especially solids, it has been found that variation of specific heat with temperature can best be expressed in the form $A + BT - CT^{-2}$, except when the value of T is small, say below 400°. (Here T is on the absolute temperature scale, degrees Kelvin.) When this expression is integrated between 0 and T to obtain the heat content above 0°K., the result is:

$$q = (A + \tfrac{1}{2}BT + CT^{-2})T. \tag{11}$$

The capital letter *C* is used as the symbol for the molal heat capacity of a substance. The heat capacity of 1 mol would be the same quantity as specific heat per mol. The small letter *c* is used as the symbol for the specific heat of 1 g. In theoretical work the molal heat capacity is of the greater significance; but in practical calculations, where weights are known in grams or kilograms, the values of *c* and c_m in calories per gram (= Calories per kilogram) are more convenient to use; the latter will therefore be given in the tables in Chap. XXV. For the same reason of convenience in use, since it is customary in practice to calculate heat contents from 0°C. as a base line, the expressions for specific heats in this book will have such values for the constants that α is the specific heat at 0°C. In many books the expressions for specific heat and heat capacity are given in the form $A + BT + CT^2$, where *T* is on the absolute scale and 0°K. (−273°C.) is the base line.

In using given values or expressions for specific heat and heat capacity, it is therefore essential to note (1) whether they are given per mol or per kilogram (or, in the case of a gas, per cubic meter) and (2) whether they are for degrees centigrade (*t*) using 0°C. as the base line or for degrees Kelvin (*T*) using 0° absolute temperature as the base line. Both methods of expression will give the same results if correctly used. More rarely, the constants given may be for the English system (B.t.u. per pound or per pound-mol and per degree Fahrenheit). The tables in this book, as is customary, use metric units; but values given in calories per gram or Calories per kilogram hold also for pound-calories per pound, and it

TABLE III.—MEAN SPECIFIC HEATS OF SOME COMMON SUBSTANCES
(In Calories per Cubic Meter for Gases, Calories per Kilogram for Solids)

Temperature interval, degrees centigrade	Air, O_2, N_2, CO	CO_2	$H_2O(g)$	C	SiO_2*	Fe
0	0.302	0.406	0.373	0.206	0.166	0.105
0–500	0.313	0.451	0.398	0.287	0.238	0.131
0–600	0.315	0.460	0.403	0.301	0.252	0.137
0–700	0.317	0.469	0.408	0.314	0.255	0.142
0–800	0.320	0.478	0.413	0.327	0.257	0.148
0–900	0.322	0.487	0.418	0.339	0.259	0.149
0–1000	0.324	0.496	0.423	0.351	0.262	0.149
0–1200	0.328	0.514	0.433	0.372	0.265	0.150
0–1500	0.335	0.541	0.448	0.399	0.275	0.149
0–1800	0.342	0.568	0.463	0.419	. .	0.21†
0–2000	0.346	0.586	0.473	0.430	.	0.21†

* R. B. SOSMAN, see Table XX, p. 398.

† For liquid iron only, above its melting point.

is recommended that problems involving specific heats, heats of reaction, etc., with weights given in pounds be worked in pound-calories instead of B.t.u. in order that values given in the tables may be used directly.

Table III gives the mean specific heats of some common substances over frequently used temperature ranges. These have been calculated from the expressions given in the tables in the back of this book and are tabulated here for ready reference.

HEAT OF REACTION AT HIGH TEMPERATURES

When the heat of a reaction is calculated from the heats of formation of the compounds involved, in the manner discussed on page 82, the result applies to the reaction at room temperature, *i.e.*, when the reacting substances are at room temperature at the beginning and the products formed are allowed to come to room temperature at the end. In other words, the calculated quantity of heat is that corresponding to a process beginning and ending at room temperature, irrespective of what temperatures may have been reached sometime during the process. This follows necessarily from the fact that heats of formation are determined and tabulated for the conditions of room temperature.

In figuring the values of heats of formation, room temperature is now usually taken as 18°C.; but for most purposes the heat of reaction so calculated may be regarded as identical with that for a temperature of 0°C. or for higher temperatures up to 35 to 40°C. If, however, the reaction represents a process beginning or ending at some elevated temperature and it is desired to know the heat liberated or required *at that temperature*, then the heat of the reaction calculated for room temperature must be suitably corrected.

As an example of a process in practice where it might be desired to know the heat of a reaction at a high temperature, consider the conversion of copper sulphide to copper metal, in accordance with the reaction

$$Cu_2S + O_2 = 2Cu + SO_2.$$

This reaction is carried out in a Bessemer converter; the temperature is 1100°C., so that the reactants (Cu_2S and O_2) are at this temperature, and also the products (Cu and SO_2). The assumption is really not a good one with respect to the oxygen and will be corrected below, but for the present let all the reacting substances be at the same temperature, so that the problem becomes one of finding the heat of this reaction at 1100°C.

First obtain the heat of the reaction at room temperature:

$$\begin{aligned} &Cu_2S + O_2 = 2Cu + SO_2. \\ \Delta H &= +18{,}950 \qquad\qquad - 70{,}940 = -51{,}990 \text{ Cal.} \end{aligned}$$

Now if the reactants are at 1100°C., when they are consumed or disappear the heat contained in them will be liberated and will serve to increase the total amount of available heat. We must therefore calculate the heat content of the Cu_2S and O_2 at 1100°C. and *add* it to the 51,990 Cal. generated. (In this summation, since heat evolved is given a negative sign, the heat in the reactants will also be given a negative sign.)

Similarly, if the products are at 1100°C. and remain at or leave the converter at that temperature, they absorb and carry away a quantity of heat equal to their heat content at 1100°C. This must accordingly be calculated and *subtracted* from the above sum.

Heat contents at 1100°:

In 160 kg. of Cu_2S:* $160 \times 0.131 \times 1,100$ =	23,050 Cal.	
Latent heat of fusion = 160×34.5 =	5,520	
In 22.4 cu. m. of O_2: $22.4(0.302 + 0.000022 \times 1,100)1,100$ =	8,030	
Total heat in reactants =	36,600 Cal.	
In 128 kg. of Cu: $128(0.0916 + 0.0000125 \times 1,083)1,083$ =	14,600 Cal.	
Latent heat of fusion = 128×41.8 =	5,360	
1083 to 1100° = $128 \times 0.079 \times 17$ =	180	
In 22.4 cu. m. of SO_2: $22.4(0.406 + 0.00009 \times 1,100)1,100$ =	12,440	
Total heat in products =	32,580 Cal.	
Heat of reaction at 1100°: $\Delta H = -51,990 - 36,600 + 32,580$ =	−56,010 Cal.	(1).

Actually the oxygen in the above reaction enters the converter in the form of unheated air. If it is desired, therefore, to learn the net amount of heat resulting from the action in the converter, the 8,030 Cal. credited as coming from oxygen should be omitted. Furthermore, since the oxygen is necessarily accompanied by nitrogen, which enters the process cold and goes out at 1100°, the heat contained in $^{79}/_{21} \times 22.4$ cu. m. of nitrogen at 1100° should be deducted.

Heat in nitrogen = $84.3(0.302 + 0.000022 \times 1,100)1,100 = 30,250$ Cal.

The *net* heat evolved in the converter as a result of the action in it is therefore $56,010 - 8,030 - 30,250 = 17,730$ Cal. (per 160 kg. of Cu_2S oxidized).

From the principles discussed above, the following rule may be formulated: **To calculate the heat of a reaction at high temperature, add the heat content of the reactants, and subtract the heat content of the products from the heat evolved in the reaction at room temperature.** This rule is to be taken in its literal algebraic sense whether the reaction is exothermic or endothermic. If the above reaction had been one which *absorbed* 51,990 Cal. at room temperature instead of liberating that quantity, we should have written in place of (1):

Heat of reaction at 1100°: $\Delta H = +51,990 - 36,600 + 32,580 = +47,970$ Cal.

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* The specific heat of liquid Cu_2S is unknown. The value 0.131 is for solid Cu_2S at 900°C.

It might be supposed that calculation of the heat of a reaction at high temperatures would be a problem with which the metallurgist is commonly concerned, since so many of his reactions are furnace processes. Actually, however, he is less often interested in this calculation. The ordinary heat of the reaction at room temperature is the more useful quantity, and the factors introduced by the furnace operation are handled separately as sources of additional heat supply or heat loss as the case may be. Thus in a smelting process the sources of heat supply might be the combustion of the fuel and heat contained in preheated blast. The items of heat loss might be heat contained in the waste gases, in the hot metal and slag produced, in cooling water, losses by radiation, convection, and conduction, etc. These would all be in addition to the heats of the smelting reactions themselves, and the latter would be taken at room temperature. By computing and enumerating all the items of heat supply and heat loss, a "heat balance sheet" of the furnace or process could be made up. This is more often the most profitable manner of studying the thermal requirements or heat economy of an operation. The heat balance is taken up in detail in later chapters.

There are, however, cases where it is desirable for the metallurgist to calculate the heat of the reaction itself at high temperatures, in the manner which has been illustrated. Such a case, for example, is in the common retort process for reduction of zinc ore, considered on page 332. The metallurgist should be aware of the principles involved and determine when such a calculation would be instructive as regards any particular process.

There are in reality five possible cases in calculating heats of reactions, *viz.*:

1. Reactants cold, products cold.
2. Reactants cold, products hot.
3. Reactants hot, products hot.
4. Reactants hot, products cold.
5. Mixed conditions: some of the reactants or products cold, others hot

The procedure in the various cases will be obvious from the foregoing discussion.

Kirchhoff's Equation.—The change in heat of reaction with change of temperature may be expressed as follows:[1]

$$dQ = (C_p - C_p')\,dt,$$

where C_p and C_p' are the heat capacities at constant pressure of the reactants and of the products, respectively, of the given reaction. In this equation all reactants and products are at the same temperature.

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[1] Kirchhoff, G., *Ann. Physik* [2], **103,** 177 (1858).

Integration of the equation and substitution of the proper values of C_p and C_p' lead to the same result as in the foregoing discussion.

Phase Symbols in Reactions.—Since the heat content of any substance taking part in a chemical reaction will depend greatly on whether it is in the solid, liquid, or gaseous state, it is desirable in some cases to follow the formula for a substance in a reaction with a symbol in parentheses to show the phase or state in which the substance is present. This should be done when any doubt can arise as to the existing state; when the state is obvious, it is better for the sake of clarity and simplicity to omit such symbols. The symbols most commonly used are:

s = solid.	c = crystalline
l = liquid.	dil = dilute solution.
g = gas.	aq = dilute aqueous solution

Others are sometimes useful. Examples of the way in which these are used are as follows:

Electrolytic extraction of copper from solution formed by leaching:

$$CuSO_4(aq) + H_2O(l) = Cu + H_2SO_4(aq) + O(g).$$

Detinning of scrap tin plate with chlorine:

$$Sn(s) + 2Cl_2(g) = SnCl_4(l).$$

Production of ammonia from cyanamide:

$$CaCN_2 + 3H_2O(g) = 2NH_3(g) + CaO + CO_2.$$

In this book, since the phase or state will usually be obvious from the nature of the process under discussion, it will not often be necessary to employ these symbols.

Problems

96. Calculate the heat of the reaction for each of the seven reactions given or required in Probs. 1 to 5. (Place the proper plus or minus sign before each answer; for CO and CO_2 use values for amorphous carbon.)

97. From the tables, Chap. XXV, obtain the following heats of formation: (Fe, Si, O_3), (FeO, SiO_2), and (Si, O_2). Write each of these in the form of a thermochemical equation. From these equations determine the heat of formation of FeO, per kilogram of Fe.

98. *a.* Given the following heats of formation (from the tables, Chap. XXV):

$$(Ag_2O,\ N_2O_5) = -46{,}100$$
$$(Ag,\ N,\ O_3) = -29{,}400.$$
$$(N_2,\ O_5) = +\ \ 600.$$

Required: The heat of oxidation of silver to Ag_2O, per kilogram of silver.

b. Given the following heats of formation ($-\Delta H$):

MnO from Mn and O: 1,757 lb.-cal. per pound of Mn.
SO_3 from S and 3O: 2,930 lb.-cal. per pound of S.
$MnSO_4$ from Mn, S, and 4O: 1,664 lb.-cal. per pound of $MnSO_4$.
Required: The molal heat of formation of $MnSO_4$ from MnO and SO_3.

99. *a.* Antimony ore containing 27 per cent Sb_2S_3 is roasted, producing Sb_2O_3 and SO_2. The weight of ore treated is 5,000 lb.

Required: 1. The volume of oxygen required, in cubic feet.

2. The quantity of heat evolved, in pound-calories.

b. An electric furnace is used to manufacture gaseous carbon bisulphide through the reaction of sulphur with carbon. The production is 7 metric tons in 24 hours.

Required: The total amount of energy evolved or required (which?) in the reaction, in Calories, and the power in kilowatts.

100. An electric furnace is supplied with CaO and C, in the proportions to form CaC_2:

$$CaO + 3C = CO + CaC_2.$$

It produces 0.25 kg. of CaC_2 per kilowatt-hour. The CaC_2 reacts with H_2O according to the reaction

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2.$$

Required: 1. The minimum power to produce 1 ton of CaC_2 per hour.

2. The electrothermal energy efficiency of the furnace operation.

3. If 100 g. of CaC_2 is treated with 10 kg. of cold H_2O, how many calories will be set free, and how many degrees rise of temperature will result?

101. *a.* Calculate the heat content (above 0°C.) of 15 kg. of tin (*a*) solid, just at the melting point; (*b*) molten, just at the melting point; (*c*) at a temperature of 1200°C.

b. Calculate the heat content (above 0°C.) of 1 mol of silicon vapor at 3700°C. (the temperature of the electric arc between carbon electrodes).

102. A coal-burning furnace was used for melting copper cathodes and required 7 hr. to melt 160 metric tons of copper. The calorific power of the coal used was 5,952 Cal. per kilogram. There was used 250 kg. of coal per ton of copper melted. The heat capacity of the gases resulting from burning 1 kg. of the coal is $4.071 + 0.000669t$. The furnace is equipped with a waste-heat boiler; temperature of the gases at the entrance to the boiler, 1100°C.; at exit from boiler, 500°C.

Required: 1. The quantity of heat required to melt the copper

2. The thermal efficiency of the furnace during the melting.

3. The boiler horsepower developed by the boiler, assuming that it utilizes 94 per cent of the heat dropped by the gases in passing through it.

103. In converting copper matte, the chemical action in each of the two stages is represented by the following equations:

$$(a)\ 2FeS + 3O_2 = 2FeO + 2SO_2.$$
$$(b)\ Cu_2S + O_2 = 2Cu + SO_2.$$

Assume that the average temperature in the converter during the first stage is 1100°C, and during the second stage 1200°C. The air, however, is blown in cold; assume that its temperature is 0°C. Calculate for the reaction only, disregarding the nitrogen, which does not appear in the reaction.

Required: 1. The heat of the first reaction, all components except oxygen being at 1100°.

2. The same for the second reaction, all components except oxygen being at 1200°C.

104. *a.* Calculate the heat of the reaction for production of silicon carbide, beginning and ending at 1700°C.:

$$SiO_2 + 3C = SiC + 2CO.$$

b. Iron carbide decomposes as follows, forming crystals of pure iron and graphite:

$$Fe_3C = 3Fe + C.$$

Required: The heat of this reaction, per pound of iron, (*a*) when it occurs in solid cast iron at a temperature of 2000°F., and (*b*) when it occurs in the production of artificial graphite at a temperature of 4000°F.

105. Calculate the heat of the reaction

$$Al_2O_3 + 3C = 2Al + 3CO,$$

taking place in the Hall process at a temperature of 1000°C. Although this temperature is below the melting point of Al_2O_3, the alumina is actually in the liquid state, being dissolved in molten cryolite. Assume, therefore, that the heat content of the Al_2O_3 includes its heat of fusion.

106. The reaction for reduction of zinc from roasted zinc ore is:

$$ZnO + C = Zn + CO.$$

Required: 1. The heat of this reaction as it takes place in the zinc retort, beginning and ending at 1000°C.

2. The heat required for the reaction, per kilogram of zinc vapor produced, allowing for the fact that the zinc oxide and carbon are put into the retort cold (assume 0°C.).

CHAPTER VI

THE IRON BLAST FURNACE

Of the various types of calculations which may be involved in the study of a furnace operation, the following are of most frequent occurrence:

I. *The Charge Balance.*—Given the components of the charge put in the furnace, including their weights and compositions, what will be the amounts and compositions of the resulting products? If the process be one of smelting or refining, these products consist in the main of the metal (or matte, in the case of some nonferrous metals), the slag, and the gases.

II. *The Charge Make-up.*—Given the compositions of various ores, fluxes, and reducing agents available, in what amounts or proportions shall these be taken to yield products of desired composition?

III. *The Heat Balance.*—With given charges undergoing known reactions and yielding certain products, what are the heat requirements, or how much heat is supplied or generated and how is it distributed? What is the thermal efficiency of the process or of the furnace? How much fuel or how much electrical energy is required?

The first of these three types of problem will be considered in this chapter, using it for study of the iron blast furnace. Calculations of products under different given conditions will be taken up first, and then a method of setting down a complete balance sheet of the furnace will be suggested. Other types of problem dealing with the iron blast furnace will follow in later chapters.

IRON SMELTING

The materials entering the iron blast furnace consist of the iron ore, the flux (limestone), and the fuel (nearly always coke), fed together at the top, and the air blown in the bottom through the tuyères. The term "charge" in common usage refers to the materials fed at the top and therefore includes the fuel; the ore and flux without the fuel is sometimes termed the "burden." The ore is an oxide of iron, and the process is essentially one of reduction of the oxide to metal by ascending CO formed by combustion of coke in the tuyère zone. Since the reaction is a reversible one, a strong reducing atmosphere must be maintained by having an excess of CO, in order that the reaction may proceed rapidly in the right direction.[1] The equation $Fe_2O_3 + 3CO = 2Fe + 3CO_2$ expresses the reduction of Fe_2O_3 by CO. To both sides of this equation a proper amount of CO should be added to represent the excess required.

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[1] See p. 216.

Reduction of Oxides.—It is to be noted that in the above reaction it is assumed that the reduction of Fe_2O_3 is performed by CO, not by C, this CO being supplied by combustion of C of the coke in the tuyère zone. Some of the carbon of the coke is consumed in reduction of silicon, manganese, and phosphorus in the smelting zone, and some by contact with iron oxides farther up in the furnace, for example:

$$
\begin{aligned}
SiO_2 + 2C &= Si + 2CO. \\
MnO + C &= Mn + CO. \\
P_2O_5 + 5C &= 2P + 5CO. \\
FeO + C &= Fe + CO. \\
2FeO + C &= 2Fe + CO_2.
\end{aligned}
$$

The reduction of iron is completed before the descending charge reaches the smelting zone. The reduction of the impurities takes place almost entirely in the smelting zone, the proportion of each reduced depending on its chemical strength at the smelting temperature. Thus most of the phosphorus on the charge is reduced, possibly half of the manganese, and perhaps a fifth of the silica, the exact proportion varying with conditions, chiefly the temperature attained. No alumina or other oxide stronger than silica is reduced.

Illustrative Problem.—The calculation of blast requirement, slag, and gases from typical blast-furnace data may now be profitably examined.

Example 8

An iron blast furnace produces pig iron of the following composition:

	Per Cent
Fe	92 8
C	3 8
Si	2 1
P	0.9
Mn	0 4

The ore smelted analyzes as follows:

	Per Cent		Per Cent
Fe_2O_3	78 0	P_2O_5	1 7
SiO_2	8 4	MgO	1 2
MnO	0 6	H_2O	5 1
Al_2O_3	5 0		

The flux amounts to one-fourth the weight of the ore and is composed of:

	Per Cent
$CaCO_3$	96
$MgCO_3$	2
SiO_2	2

The coke used is 900 kg. per ton of pig iron and contains:

	Per Cent
C	88
SiO_2	9
Al_2O_3	1
H_2O	2

The gases carry 2 parts of CO to 1 part CO_2.

Assume that 99.5 per cent of the iron is reduced, 0.5 per cent slagged.

Required: Per ton (1,000 kg.) of pig iron made:

1. The weight of ore used.
2. The weight of slag made, and its percentage composition.
3. The volume of air required.
4. The volume and percentage composition of the blast-furnace gas.

Solution:

Fe in 1 kg. of ore = $\frac{112}{160} \times 0.78 = 0.546$ kg. Of this, $0.005 \times 0.546 = 0.0027$ kg. is slagged and 0.5433 kg. reduced.

The weight of ore then = $\frac{928}{0.5433}$ = 1,708 kg. (1).

Total SiO_2 charged = $(0.084 \times 1{,}708) + (0.02 \times \frac{1}{4} \times 1{,}708) + (0.09 \times 900)$ = 233 kg.

SiO_2 reduced to Si = $\frac{60}{28} \times 21 = 45$ kg.
SiO_2 in slag = 233 − 45 = 188 kg.
MnO in slag = $(0.006 \times 1{,}708) - \frac{71}{55} \times 4 = 5$ kg.
P_2O_5 in slag = $(0.017 \times 1{,}708) - \frac{142}{62} \times 9 = 8$ kg
FeO in slag = $\frac{72}{56} \times \frac{5}{995} \times 928 = 6$ kg
Al_2O_3 = $(0.05 \times 1{,}708) + (0.01 \times 900)$ = ~~94 kg.~~ 85.4 + 9 = 94.4 kgs
MgO = $(0.012 \times 1{,}708) + (\frac{40}{84} \times 0.02 \times \frac{1}{4} \times 1{,}708)$ = 25 kg.
CaO in slag = $\frac{56}{100} \times 0.96 \times 427 = 229$ kg.

Summary of slag:

SiO_2 =	188 kg	=	33 9 per cent
MnO =	5	=	0 9
P_2O_5 =	8	=	1 4
CaO =	229	=	41 3
FeO =	6	=	1 1
MgO =	25	=	4.5
Al_2O_3 =	94	=	16 9
	555 kg.	=	100 0 per cent (2)

Total C in gases = $(0.88 \times 900) + (\frac{12}{100} \times 0.96 \times 427) + (\frac{12}{84} \times 0.02 \times 427) - 38$ = 804 kg .4
= 792 + 49.2 + 1.2 − 38 = 804.4 kg.

Of this, since CO and CO_2 contain one atom of carbon each, $\frac{2}{3}$ goes to CO and $\frac{1}{3}$ to CO_2.

O required for CO = $\frac{2}{3} \times 804 \times \frac{16}{12}$ = 718 kg.
O required for CO_2 = $\frac{1}{3} \times 804 \times \frac{32}{12}$ = 718
Total = 1,436 kg.

But part of this O is already present in combination with the C of the flux, and part is obtained by reduction of the oxides in the ore:

$$\text{O with C of flux} = \tfrac{32}{12}(49.2 + 1.2) = 134 \text{ kg.}$$

$$\text{O in } Fe_2O_3 = \tfrac{48}{160} \times 0.78 \times 1{,}708 = 400 \text{ kg.}$$

$$\text{O in FeO in slag} = \tfrac{16}{72} \times 6 = \underline{\quad 1 \quad}$$

$$\text{O derived from reduction of iron} = 399$$

$$\text{O from reduction of } SiO_2 = \tfrac{32}{28} \times 21 = 24$$

$$\text{O from reduction of MnO} = \tfrac{16}{55} \times 4 = 1$$

$$\text{O from reduction of } P_2O_5 = \tfrac{80}{62} \times 9 = 12$$

$$\text{Total O available from charge} = 570 \text{ kg.}$$

Oxygen to be supplied from air = 1,436 − 570 = 866 kg

$$\text{Weight of blast} = \frac{866}{0.232} = 3{,}730 \text{ kg.}$$

$$\text{Volume of blast} = \frac{3{,}730}{1.293} = 2{,}885 \text{ cu. m. (3).}$$

Blast-furnace gas:

$$CO = \frac{28}{16} \times 718 \times \frac{22.4}{28} = 1{,}005 \text{ cu. m} = 25.7 \text{ per cent}$$

$$CO_2 = \frac{44}{32} \times 718 \times \frac{22.4}{44} = 503 = 12.9$$

$$N_2 = 0.79 \times 2{,}885 = 2{,}278 = 58.1$$

$$H_2O = (0.051 \times 1{,}708 + 0.02 \times 900)\frac{22.4}{18} = 131 = 3.3$$

$$3{,}917 \text{ cu. m.} = 100.0 \text{ per cent (4)}$$

In the above problem it has been assumed that the $CaCO_3$ decomposes into CaO and CO_2 and that the resulting CO_2 enters the gases as such. Actually a large part of this CO_2 will be reduced to CO by reaction with carbon, this reduction readily taking place at temperatures below those at which $CaCO_3$ breaks up rapidly. But, so far as the furnace as a whole is concerned, it is entirely immaterial whether such reduction takes place or not. For with a given amount of carbon and a given amount of oxygen entering, the final result, both as to composition of products and as to amount of heat used, is the same regardless of intermediate reactions. The assumption was therefore a proper one; but if study were made of a particular zone in the furnace instead of the furnace as a whole, the reaction between coke and the CO_2 of the limestone might need to be taken into account.

Consumption of Carbon before the Tuyères.—The oxygen in the blast penetrates but a short distance above the tuyère level. It is all consumed in burning the carbon of the coke to CO. Most of the carbon in the coke descends through the shaft of the furnace until it reaches the tuyère zone, where it is met by the blast and burned to carbon monoxide. The high temperature precludes the formation of carbon dioxide.[1] Some of the carbon, however, through actual contact with iron oxide, is oxidized (either to CO or CO_2) in the upper part of the furnace. This oxidation, of course, liberates heat above, instead of in, the smelting zone where it is most needed and likewise tends to decrease the proportion of carbon fully oxidized to CO_2 in the furnace and thereby the quantity of heat developed in the furnace. Grüner, many years ago, put forth the theory that in the ideal working of an iron blast furnace all the carbon would be burned at the tuyères and none above. If the amount of blast is known, the quantity of carbon burned at the tuyères may easily be calculated from the reaction $2C + O_2 = 2CO$. This calculation is often useful in checking the performance of a blast furnace.

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[1] STOUGHTON, BRADLEY, and ALLISON BUTTS, "Engineering Metallurgy," 3d ed., pp. 71–74, McGraw-Hill Book Company, Inc., New York, 1938.

Example 9

In Example 8, the volume of the blast per ton of pig iron was found to be 2,885 cu. m. The coke used per ton of pig iron was 900 kg. containing 88 per cent carbon.

Calculate the percentage of the carbon of the coke that is burned at the tuyères.

Solution:

$$2C + O_2 = 2CO.$$

2,885 cu. m. of air contains $0.21 \times 2,885 = 606$ cu. m. of O_2.

This consumes $606 \times \frac{24}{22.4} = 649$ kg. of carbon.

The coke contains $0.88 \times 900 = 792$ kg.

Therefore, $^{649}/_{792}$, or 82.0 per cent, of the carbon is burned at the tuyères.

Of the remaining carbon, part is oxidized above the tuyères by contact with iron oxide, and part enters the pig iron.

The Reduction Equation and Theoretical Coke Consumption.—In the representative equation

$$Fe_2O_3 + xCO = 2Fe + 3CO_2 + (x - 3)CO$$

the ratio of CO to CO_2, $\frac{x - 3}{3}$, must always be high and will usually be between 1.5 and 2.0.*

Let it be supposed that the furnace operator desires the ratio of CO to CO_2 to be 1.8:1, ignoring for the present the additional CO_2 that will be supplied by decomposition of limestone ($CaCO_3 \rightarrow CaO + CO_2$), and let it be required to obtain:

1. The value of x in the above equation.
2. The weight of carbon required, per ton of iron reduced.
3. The volume of air required, per ton of iron reduced.

Solution:

$$\frac{x - 3}{3} = \frac{1.8}{1}, \text{ whence } x = 8.4 \text{ (1).}$$

The equation becomes: $Fe_2O_3 + 8.4CO = 2Fe + 3CO_2 + 5.4CO$. From this equation it is evident that 2Fe requires 8.4C, or 112 kg. of Fe requires 100.8 kg. of C. Then 1 ton of iron (1,000 kg.) requires $\frac{1,000}{112} \times 100.8 = 900$ kg. of C (2).

---

* Formerly it was often higher than 2.5:1. In the best modern practice it is about 1.5:1, and it is predicted that through proper charging methods 1:1 may be attained.

The 8.4C is combined with 8.4O, or, by weight, 16 parts O to 12 parts C. The oxygen required is therefore:

$$\tfrac{16}{12} \times 900 = 1{,}200 \text{ kg.}$$

$$\frac{1{,}200}{0.232} \div 1.293 = 4{,}000 \text{ cu. m. of air per ton of iron (3).}$$

When the amount of $CaCO_3$ used as flux is known, it is necessary to take into account the CO_2 liberated from it. This is best done by finding the carbon content of the $CaCO_3$ and adding it to the carbon obtained from the coke *before* converting the carbon to CO and CO_2 in the proper proportions. In finding the air requirement, allowance must then be made for the fact that the carbon from the limestone requires no air, having entered as CO_2.

When the carbon content of the pig iron is known, the amount of carbon thus absorbed by the iron must be deducted to obtain the total carbon available for the gases

Assume that in the foregoing example the pig iron would contain 93 per cent Fe and 4 per cent C. Assume also that 300 kg. of $CaCO_3$ was charged, per ton of Fe reduced

The 300 kg. of $CaCO_3$ will liberate $\tfrac{44}{100} \times 300 = 132$ kg. of CO_2 per 1,000 kg. of Fe reduced, or 14.8 kg. per 112 kg. of Fe reduced. This is $\frac{14.8}{44} = 0.34$ kg.-mol for 2 kg.-mols of Fe, making the total number of molecules of CO_2 in the original reaction 3.34 instead of 3. Then $\frac{x - 3}{3.34} = \frac{1.8}{1}$, whence $x = 9.0$. The equation might be written $Fe_2O_3 + 9CO + 0.34CO_2 = 2Fe + 3.34CO_2 + 6CO$, and the computations made from this point in the same manner as before, with the addition of $\tfrac{4}{93} \times 1{,}000$, or 43 kg. of C to the total C requirement to allow for that absorbed by the pig iron. The result is 1,008 kg. of carbon required per ton of Fe, or 937 kg. per ton of pig iron containing 93 per cent Fe.

Production and Utilization of the Blast-furnace Gas.—With respect to the combustion of its fuel and the resultant formation of gases, the iron blast furnace is like a huge gas producer. There is always an excess of carbon in the combustion zone, and the product formed from it is CO. There is, of course, no steam blown in as such, but whatever moisture is present in the blast is decomposed by carbon as in the gas producer:

$$H_2O + C = CO + H_2.$$

Added to this hydrogen are any hydrogen and other volatile matter expelled from the coke, these two sources accounting for the small percentage of hydrogen and CH_4 found in blast-furnace gas. It must be noted that the furnace charge enters at the top and undergoes a gradual heating as it descends slowly in the furnace, while the blast enters directly the hottest part. Moisture in the ore, flux, and coke is evaporated in the upper part of the furnace and enters the gas as H_2O vapor.

Blast-furnace gas is accordingly combustible, though of much lower heating value than producer gas. The high temperature required in the blast furnace necessitates using preheated blast. Burning a portion of the blast-furnace gas in "hot-blast stoves" constitutes a convenient and cheap method of heating the blast. The stove receives a portion of the gas and burns it, thus heating the refractory material of which the interior of the stove is constructed. The supply of gas is now diverted to heat another stove, and the cold blast is run through the heated stove on its way to the furnace, taking up heat from the stove until the latter has cooled to the point where it must again be supplied with gas and go through the heating cycle.

Less than half of the gas made by the furnace is needed to heat the blast. The remainder of the gas is available for production of power. This was formerly done by burning the gas under steam boilers but is now more often accomplished by using the gas directly in internal-combustion engines.

Two examples will now be given, the first illustrating the calculation of the amount of gas made and the utilization of it, the second illustrating the calculation of the temperature attained by the gases in the combustion zone of the blast furnace.

Example 10

A blast furnace produces per day 500 tons of pig iron containing 4 per cent carbon It uses 0.85 ton of coke per ton of pig iron, the coke being 90 per cent carbon It uses also 250 kg of $CaCO_3$ per ton of pig iron; the charge contains no other carbonates.

The blast-furnace gas analyzes:

	Per Cent
CO_2	12
CO	24
N_2	60
H_2O	4

The blast is preheated to 600°C. in stoves having a thermal efficiency of 60 per cent.[1] The gas not required by the stoves is used in gas engines at a thermomechanical efficiency of 25 per cent.

Required. 1. The volume of gas made, per day.

2. The volume of the blast (assumed dry).

3. The proportion of the gas required by the stoves.

4. The power generated in the gas engines.

5. The percentage of the heating value of the coke that is developed in the furnace

Solution:

$$0.90 \times 0.85 \times 500 = 382 \text{ tons of C in the coke.}$$

$$^{12}/_{100} \times 0.250 \times 500 = 15 \text{ tons of C in the flux.}$$

$$0.04 \times 500 = 20 \text{ tons of C in the pig iron}$$

$$382 + 15 - 20 = 377 \text{ tons of C in the gases.}$$

---

[1] The thermal efficiency of a clean stove using well-cleaned gas may exceed 75 per cent, falling off as dust collects.

$$1 \text{ cu. m. of gas will contain } \frac{12}{22.4}(0.12 + 0.24) = 0.193 \text{ kg. of C.}$$

$$\frac{377{,}000}{0.193} = 1{,}950{,}000 \text{ cu. m. of gas made (1).}$$

$$0.60 \times 1{,}950{,}000 = 1{,}170{,}000 \text{ cu. m. } N_2.$$

$$\frac{1{,}170{,}000}{0.79} = 1{,}480{,}000 \text{ cu. m. of blast (2).}$$

At 600°C. this blast will contain

$$1{,}480{,}000(0.302 + 0.000022 \times 600)600 = 280{,}000{,}000 \text{ Cal.}$$

This heat is to be supplied by stoves 60 per cent efficient; the heating value of the fuel supplied to the stoves is therefore $\frac{280{,}000{,}000}{0.60} = 467{,}000{,}000$ Cal.

The heating value of 1 cu. m. of the gas is

$$0.24 \times 3{,}034 = 728 \text{ Cal.}$$

$$\frac{467{,}000{,}000}{728} = 642{,}000 \text{ cu. m. of gas required}$$

$$\frac{642{,}000}{1{,}950{,}000} = 32.9 \text{ per cent of the gas is required (3).}$$

The gas left over is 1,950,000 − 642,000 = 1,308,000 cu. m.

Its heating value is 728 × 1,308,000 = 952,000,000 Cal. per day, or $\frac{952{,}000{,}000}{24}$ = 39,700,000 Cal. per hour.

860 Cal. per hour = 1 kw.

The power generated is therefore $0.25 \times \frac{39{,}700{,}000}{860} = 11{,}530$ kw. (4).

The heating value of the coke is 382,000 × 8,100 = 3,094,000,000 Cal. All this heat except that left in the gas and that represented by the carbon in the pig iron may be regarded as having been liberated in the furnace

Heating value of the gas	= 1,950,000 × 728	=	1,420,000,000 Cal
Heating value of carbon in pig iron	= 20,000 × 8,100	=	162,000,000
			1,582,000,000 Cal.

Heat developed in furnace = 3,094,000,000 − 1,582,000,000 = 1,512,000,000 Cal.

$$\frac{1{,}512}{3{,}094} = 48.9 \text{ per cent (5).}$$

Of the power generated from the blast-furnace gas, the operations of the furnace itself require a portion, chiefly for the "blowing engines" which compress the blast. Calculation of the power requirement for this purpose is discussed in Chap. VIII.

Coke Consumption in the Iron Blast Furnace.—The amount of coke consumed in an iron blast furnace is frequently stated as approximating "a ton of coke per ton of pig." This is nearly true so far as gross consumption goes, *i.e.*, the amount of coke actually charged to the furnace, and is a fact easy to remember. In large modern furnaces the gross consumption is somewhat less than this, the amount required depending on the chemical composition of the ore, the physical character of the ore, and a number of other factors which cannot be discussed here.

In reverberatory copper smelting and a number of other processes, where either sensible or latent heat contained in the waste gases is extracted and utilized, it is common in referring to the fuel consumption of the furnace to mean, not the gross amount of fuel burned, but the net amount required by the furnace after crediting the heat recovered in waste-heat boilers or by other means. Since iron-blast-furnace gas is combustible and there is always an excess over that needed by the stoves to heat the blast for the furnace itself, the excess being available and always utilized for production of power or steam, this available excess of heat may be credited to the furnace and the *net* consumption of coke determined.

In the example immediately preceding, the heating value of the gas used for power production was 952,000,000 Cal. per day, equivalent to 31 per cent of the heating value of the coke. If one-third the power generated is required by the furnace itself to compress its blast, operate its charging skips, etc., there is left excess power equivalent to about 20 per cent of the heating value of the coke. Consequently, the *net* coke consumption is only 0.65 ton of coke, instead of 0.85 ton, per ton of pig iron.

The blast-furnace manager is greatly interested in reducing both the gross and the net coke consumption to as low a figure as is possible with satisfactory operation of the furnace. Further light on coke consumption may be gained from the heat balance of the iron blast furnace given in Chap. IX.

Maximum Theoretical Temperature in the Blast Furnace.—The maximum temperature attained in the smelting zone may be calculated (though only approximately) in accordance with the principles already outlined on page 31, in connection with complete combustion. In the blast furnace a different condition exists with reference to the fuel just before combustion. The coke has been gradually heating during its slow descent through the furnace, receiving the heat from the gases *after they have left the zone of combustion.* Thus the fuel enters the combustion process, not in a virtually cold condition as in combustion on an ordinary grate, but preheated to a temperature not far below the maximum actually attained by the combustion. As this temperature is nearly the same as that under calculation—the temperature designated by the unknown t—it may be assumed that the coke is preheated to $t°$ in rough calculations or perhaps to $t - 300°$ for a somewhat closer estimation.

A further difference exists with respect to the behavior of hydrogen in the fuel and moisture in the blast. As noted above, moisture in the blast will act like steam in a gas producer. The H_2O is decomposed by carbon, absorbing heat and thereby reducing the temperature of the combustion. From this reaction it also becomes evident that hydrogen, whether from this source or present in the coke, will not burn to H_2O in the smelting zone, although some of it may go to H_2O farther up in the furnace through reaction with iron oxide.

Example 11

The average atmospheric conditions at Bethlehem, Pa., during the months of January and July, 1927, were as follows:

January: temperature, −1°C.; pressure, 754 mm.; humidity, 78 per cent
July: temperature, 24°C.; pressure, 747 mm.; humidity, 68 per cent.

Assume that the moisture content of the air entering a Bethlehem blast furnace corresponds to the conditions stated. Assume that the carbon is the only constituent of the coke which burns, that it is preheated to a temperature 300°C. below the maximum temperature attained by the gases in the combustion zone, and that the noncombustible constituents of the coke carry into the smelting zone the same amount of heat which they carry out. The blast is preheated to 750°C.

Required: 1. The maximum theoretical temperature in the tuyère zone, assuming the blast dry.

2. The grams of water vapor carried in the air, per kilogram of carbon burned, and the percentage of the heat developed by the combustion of the carbon which is required to decompose this water vapor, for the conditions of January and of July.

3. The maximum theoretical temperature in the tuyère zone under each of these conditions.

Solution: The heat produced by C burning to CO is 2,430 Cal per kilogram. The volume of air required per kilogram of carbon, obtained from the equation

$$2C + O_2 = 2CO,$$

is $\frac{22.4}{24} \div 0.21 = 4.444$ cu. m.

The volumes of the resulting gases are $\frac{44.8}{24} = 1.866$ cu. m. of CO, and $0.79 \times 4.444 = 3.511$ cu. m. of N_2.

The mean specific heat of CO, N_2, and air is $0.302 + 0.000022t$ per cubic meter. The mean specific heat of carbon is $0.20 + 0.00018t - 0.000000033t^2$ per kilogram.

The total heat available and liberated in the combustion will be the sum of the heat content of the carbon + the heat content of the preheated air + 2,430. This is to be equated to the heat content of the resulting gases at the temperature t.

$$1[0.20 + 0.00018(t - 300) - 0.000000033(t - 300)^2](t - 300) + 4.444(0.302 + 0.000022 \times 750)750 + 2{,}430 = (1.866 + 3.511)(0.302 + 0.000022t)t.$$

This equation may now be solved for t. However, it is an equation of the third degree owing to the t^2 term in the specific heat of carbon. This term is evidently not of large value, and the solution of a cubic equation can be avoided without introducing an appreciable error by assuming *for this term only* a value of 2,000 for one of the t's, so that the expression for the specific heat of carbon (in the vicinity of 2000°) becomes $0.20 + 0.00011t$. The above equation then becomes:

$$1[0.20 + 0.00011(t - 300)](t - 300) + 4.444(0.302 + 0.000022 \times 750)750$$
$$+ 2{,}430 = 5.377(0.302 + 0.000022t)t.$$

Simplifying:

$$0.0000083t^2 + 1.49t - 3{,}441 = 0$$
$$t = 2310°\text{C. (1).}$$

NOTE: If the temperature to which the coke is preheated be taken as t instead of $(t - 300)$, the result is $t = 2440°$.

Aqueous vapor pressure at -1°C. = 4.2 mm.

$$0.78 \times 4.2 = 3.3 \text{ mm. of } H_2O \text{ in total pressure of 754 mm.}$$

$$\frac{3.3}{754 - 3.3} \times 4.444 = 0.0195 \text{ cu. m.}$$

$0.0195 \times 1{,}000 \times \frac{18}{22.4} = 15.7$ g. of water vapor in the air per kilogram of carbon burned in January (2a).

Aqueous vapor pressure at 24°C. = 22.3 mm.

$$0.68 \times 22.3 = 15.2 \text{ mm. of } H_2O \text{ in total pressure of 747 mm.}$$

$$\frac{15.2}{747 - 15.2} \times 4.444 = 0.0924 \text{ cu. m.}$$

$0.0924 \times 1{,}000 \times \frac{18}{22.4} = 74.3$ g. of water vapor in the air in July (2b).

NOTE: These quantities are equivalent to 7.85 tons of water each 24 hr. in the blast of a furnace using 500 tons of coke in 24 hr in January, and 37.1 tons of water each 24 hr. in July.

The heat of formation of water vapor is 57,840 Cal per kilogram-mol., or 3,210 Cal. per kilogram.

To decompose 15.7 g. of H_2O vapor, therefore, requires $0.0157 \times 3{,}210 = 50$ Cal.

To decompose 74.3 g. requires $0.0743 \times 3{,}210 = 239$ Cal.

These quantities are $\frac{50}{2{,}430}$ and $\frac{239}{2{,}430}$, or 2.06 per cent and 9.8 per cent of the heat produced by the coke for January and July, respectively (2c).

In calculating the theoretical temperature at the tuyères under the January conditions, 50 Cal. must be subtracted from the 2,430 yielded by the carbon. Also, there will be a small change in the air required and the gases produced, since some of the carbon will be burned by the H_2O instead of by air. It will be instructive to follow the calculation through, taking these changes into account.

The C burned by the 15.7 g. of H_2O will be $0.0157 \times {}^{12}\!/_{18} = 0.0105$ kg., leaving 0.9895 kg. burned by air. The dry air required is therefore $0.9895 \times 4.444 = 4.397$ cu. m., and the N_2 will be $0.79 \times 4.397 = 3.474$ cu. m. Since all the C goes to CO whether burned by air or by H_2O, the volume of CO formed will be unchanged. The decomposition of H_2O will form 22.4 cu. m. of H_2 for every 18 kg. of H_2O, or a total of $0.0157 \times \frac{22.4}{18} = 0.0195$ cu. m. of H_2. The specific heat of H_2 is $0.301 + 0.000020t$, a value which is so close to that for CO, O_2, and N_2 that *small amounts* of H_2 may be included with these gases in calculating the total heat capacity of a mixture. The total volume of gases is then $3.474 + 1.866 + 0.019 = 5.359$ cu. m.

The equation for t then becomes:

$$1[0.20 + 0.00011(t - 300)](t - 300) + 4.397(0.302 + 0.000022 \times 750)750 + 0.0195$$
$$(0.373 + 0.000050 \times 750)750 + 2{,}430 - 50 = 5.359(0.302 + 0.000022t)t$$

Simplifying:

$$0.0000079t^2 + 1.484t - 3{,}386 = 0.$$
$$t = 2250°\text{C. (January)}$$

$0.0743 \times \frac{12}{18} = 0.0495$ kg. of C burned by H_2O, leaving 0.9505 by air. $0.9505 \times 4.444 = 4.224$ cu. m. of air required.

$N_2 = 0.79 \times 4.224 = 3.335$ cu. m.

$0.0743 \times \frac{22.4}{18} = 0.0925$ cu. m. H_2O and H_2.

The equation is:

$$1[0.20 + 0.00011(t - 300)](t - 300) + 4.224(0.302 + 0.000022 \times 750)750 + 0.0925(0.373 + 0.000050 \times 750)750 + 2{,}430 - 239 = 5.293(0.302 + 0.000022t)t.$$

Simplifying:

$$0.0000064t^2 + 1.464t - 3{,}178 = 0.$$
$$t = 2130°\text{C. (July)}.$$

J. W. Richards calculated and tabulated the theoretical maximum temperature before the tuyères for various blast temperatures from 40 to 1000°C. combined with various moisture contents from 5 to 40 g. per cubic meter of blast.[1]

Critical Hearth Temperature, Coke Consumption, and Smelting Power.—The consumption of coke per ton of pig iron depends on the temperature of the blast, because the higher its temperature the more heat it supplies and the less heat must come from the coke; likewise, it depends on the moisture content of the blast, since the greater the amount of moisture the more heat is used in decomposing it. It was shown by J. E. Johnson, Jr.,[2] that the coke consumption is roughly inversely proportional, not to the *total* heat content of the gases in the smelting zone, but to the *excess* heat represented by the heat supplied in combustion (including sensible heat in the coke and in the blast) *minus* the heat content of the gases at a certain "critical temperature" which is determined by the "free-running temperature of the slag." This temperature varies somewhat with different furnaces and charges but is usually sufficiently close to 2750°F. or 1500°C. to permit general use of one of these figures in calculations. As an example, suppose the heat content of the gases per pound of coke burned is 4,100 B.t.u. at 2750°F. and, when the heat supplied in combustion is 5,000 B.t.u. per pound of coke, the coke consumption is 2,000 lb. per ton of pig iron. Now if the heat supplied rises to 5,100 B.t.u., the *available* hearth heat has increased from 900 to 1,000 B.t.u., and the coke consumption would then fall from 2,000 lb. to about $\frac{900}{1{,}000} \times 2{,}000 = 1{,}800$ lb. Johnson calculated the data for a diagram showing the available hearth heats above different critical temperatures for blasts of various temperatures and moisture contents.

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[1] "Metallurgical Calculations," p. 312, McGraw-Hill Book Company, Inc., New York, 1918.

[2] "The Principles, Operation, and Products of the Blast Furnace," pp. 30–47, McGraw-Hill Book Company, Inc., New York, 1918.

Although Johnson's discussion was confined to coke consumption, this principle may be extended to the question of rate of furnace driving or rate of pig-iron production in a given furnace. This rate varies with the physical condition of the charge, furnace design, blast conditions, and other factors; but, assuming all these factors equal, it will depend on the amount of coke burned per unit time. The ratio of weight of coke to weight of pig iron can obviously be reduced either by keeping the rate of pig production constant while reducing the rate of burning coke or by continuing to supply coke at the same rate while increasing the rate of pig production. The available hearth heat per ton of pig iron may be termed the *smelting power* of the furnace. The ratio of change in smelting power caused by change in the temperature or moisture content of the blast, coke consumption per ton of pig iron remaining constant, is the same as the ratio of change in coke consumption per ton of pig iron, rate of pig production remaining constant, but in the opposite direction. Either ratio is determined by the ratio of change in the amount of heat available above the critical hearth temperature.

Instead of using the ratio of change in the available hearth heats, the ratio of change in the temperature difference between the maximum theoretical temperature at the tuyères and the critical hearth temperature may be used as a good approximation except when the composition of the furnace gases is considerably changed.

In practice, the rate of driving is sometimes increased either by increasing the coke consumption or by increasing the temperature of the blast (although the extent to which this can be done is, of course, limited). The process of drying the blast, which was first used by James Gayley in 1904, has not been widely adopted because of the cost of drying and also because most blast-furnace men have been content with raising the blast temperature. However, increased consideration is now being given to this method. Problems 134 to 137 illustrate the effect of moisture content of the blast.

Use of Oxygen-enriched Air.—Another method of increasing the available hearth heat is by using blast enriched in oxygen above the normal 21 per cent. This reduces the amount of nitrogen in the blast and thus reduces the heat content of the gases at the critical hearth temperature. It also raises the temperature attained at the tuyères from a given supply of heat in combustion. This method has been used only experimentally because there is as yet no sufficiently economical way of obtaining the oxygen-enriched blast. Experimental work has shown notable improvement in coke consumption and rate of pig-iron production. The maximum temperature would be obtained by using pure oxygen, but too high a temperature would not be desirable. For economic reasons also, 26 to 31 per cent oxygen have been the percentages tried. A considerable amount of nitrogen is also desired because of its function of carrying the heat up the shaft and thus preheating the descending charge. Problems 132 and 138 illustrate the effect of oxygen enrichment.

The Furnace Charge Balance.—When the amounts and analyses of the different components of a furnace charge are known, it is often useful to set down a formal listing of the various items of charge (ingoing material), and opposite them the various items of products (outgoing material), in the form of a balance sheet. The sum of the weights of the various items in the charge column shows the total weight of material entering the furnace. The sum of the weights of the items in any of the product columns shows the total weight of that product. In the complete balance, the sum of the various product columns equals the total of the charge column. It is recommended that the balance be preserved with respect to *each item, i.e.*, that the distribution of each item of charge to the different products be shown in such a manner that the sum of the products equals the weight of the charge in the case of each item as well as in the case of the totals.

The exact form of the balance sheet may be varied to suit the individual. A desirable form will be shown in the following example. It will be noted that no attempt is made to indicate the form or combination in which a given element enters a given product; only the weight distribution is shown. After the balance sheet is completed, it is then a fairly simple matter to compute from it the weights according to compounds and the percentage composition of the various products. It is desirable, in order to avoid errors and to make the balance sheet readily intelligible, to enter in the balance sheet the symbol of each element or compound beside its weight.

In many cases, where there are two or more items containing a given element, it is manifestly impossible to know the exact distribution of each. For example, it may be known that the slag contains 50 kg. of iron, but it will not be known whether this iron in the slag came from Fe_2O_3 in the ore, or from FeO in the limestone, or from FeS in the coke. All that can be done in such cases is to see that the right total amount is entered in the proper column, taking it from whatever source is most probable or involves the least confusion in making the computations.

Example 12

An iron blast furnace smelting a magnetite ore uses per day 912 short tons of ore, 510 tons of coke, and enough limestone to yield a slag of 40 per cent SiO_2. Assume that all the phosphorus, one-half the manganese, and one-fifth the silicon charged are reduced and go into the pig iron, which also contains by analysis 4 per cent carbon. Assume all the sulphur slagged as CaS. 1 per cent of the iron charged is lost in the slag. The blast amounts to 112,000 cu. ft. (measured at 60°F., 30 in. pressure) containing 9 grains of moisture per cubic foot, per ton of coke charged.

The analyses of the ore, flux, and coke are as follows:

Ore, per cent		Flux, per cent		Coke, per cent	
Fe_3O_4	70.3	$CaCO_3$	95.4	C	87.2
Fe_2O_3	4.8	$MgCO_3$	2.5	SiO_2	9.0
SiO_2	10.2	Al_2O_3	0.5	FeS	2.0
P_2O_5	0.9	SiO_2	0.9	H_2O	1.8
MnO_2	3.6	H_2O	0.7		
Al_2O_3	2.6				
H_2O	7.6				

Required: 1. A complete charge balance sheet of the furnace, in pounds per day.

2. The percentage composition of the pig iron, the slag, and the gases.

Solution: Enter the weights of the components of the ore and coke in the charge column of the balance sheet, below.

Fe in Fe_3O_4 = $\frac{168}{232} \times 1{,}281$ = 928 (thousand pounds)
Fe in FeS of coke = $\frac{56}{88} \times 20$ = 13
Fe in Fe_2O_3 = $\frac{112}{160} \times 88$ = 62
Total Fe charged = 1,003 (thousand pounds)

$0.01 \times 1{,}003 = 10$ Fe lost in slag (as FeO). $\frac{72}{56} \times 10 = 13$ FeO. Assume this taken from the Fe_2O_3. $62 - 10 = 52$ Fe enters the pig from Fe_2O_3.

Mn in MnO_2 = $\frac{55}{87} \times 66 = 42$. Mn in pig = 21. MnO in slag = $\frac{71}{55} \times 21 = 27$.

Before calculating the SiO_2 it will be necessary to determine the weight of the flux, since the flux contains SiO_2. If the weight of the flux be taken as x, the SiO_2 in it will be $0.009x$ and the total SiO_2 charged $186 + 92 + 0.009x$, four-fifths of which enters the slag and constitutes 40 per cent thereof. The other components of the slag are as follows:

From the ore: FeO + MnO + Al_2O_3 = 13 + 27 + 47 = 87.

From the flux: CaO + MgO + Al_2O_3 = $0.534x + 0.012x + 0.005x = 0.551x$.

From the coke: CaS, formed from FeS by using some of the CaO of the flux (FeS + CaO + C = Fe + CaS + CO), = $\frac{72}{88} \times 20 = 16$. CaO used = $\frac{56}{88} \times 20 = 13$.

Total weight of slag, including SiO_2 = $87 + (16 - 13) + 0.551x + \frac{4}{5}(278 + 0.009x) = 312 + 0.558x$.

Then:

$$222 + 0.007x = 0.40(312 + 0.558x),$$

whence

$$x = 449.$$

This may now be entered in the balance sheet. The total SiO_2 charged is $278 + 0.009x = 282$. Si in pig iron = $\frac{28}{60} \times \frac{282}{5} = 26$.

CaO in flux = $\frac{56}{100} \times 429 = 240$. CaO needed to form CaS = $\frac{56}{88} \times 20 = 13$. Ca = $\frac{40}{56} \times 13 = 9$.

Total weight of pig iron without carbon = 1,047. Weight of C = $\frac{4}{96} \times 1{,}047 = 44$.

Total blast = 510 × 112,000 = 57,100,000 cu. ft. at 60°, 30 in. H_2O in this = 9 × 57,100,000 = 514,000,000 grains = 73,400 lb. One pound-molecular weight of a gas occupies 359 cu. ft. at 0°C., 760 mm., or $359 \times \frac{273 + 15.5}{273} \times \frac{760}{762} = 378$ cu. ft. at 60°F., 30 in. 73,400 lb. of $H_2O = \frac{73,400}{18} \times 378 = 1,540,000$ cu. ft. Volume of dry air = 57,100,000 − 1,540,000 = 55,560,000 cu. ft. 1 cu. ft. of air at 0°C., 760 mm., weighs 0.0807 lb., or 1 cu. ft at 60°F., 30 in., weighs $0.0807 \times \frac{273}{285.5} \times \frac{762}{760} =$ 0.07737 cu. ft.

55,560,000 × 0.07737 = 4,300,000 lb. of dry air.

0.232 × 4,300,000 = 997,600 lb. of oxygen.

CHARGE BALANCE SHEET

(In pounds per day divided by 1,000)

Charge	Pig iron	Slag	Gases
Ore (1,824):			
Fe_3O_4 = 1,281	Fe = 928		O = 353
Fe_2O_3 = 88	Fe = 52	FeO = 13	O = 23
SiO_2 = 186	Si = 26	SiO_2 = 130	O = 30
P_2O_5 = 16	P = 7		O = 9
MnO_2 = 66	Mn = 21	MnO = 27	O = 18
Al_2O_3 = 47		Al_2O_3 = 47	
H_2O = 138			H_2O = 138
Flux (449):			
$CaCO_3$ = 429		CaO = 227	CO_2 = 189
		Ca = 9	O = 4
$MgCO_3$ = 11		MgO = 5	CO_2 = 6
Al_2O_3 = 2		Al_2O_3 = 2	
SiO_2 = 4		SiO_2 = 4	
H_2O = 3			H_2O = 3
Coke (1,020):			
C = 890	C = 11		C = 846
SiO_2 = 92		SiO_2 = 92	
FeS = 20	Fe = 13	S = 7	
H_2O = 18			H_2O = 18
Blast (4,373):			
O = 998			O = 998
N = 3,302			N = 3,302
H_2O = 73			H = 8
			O = 65
Totals 7,664	1,091	563	6,010

The balance sheet may now readily be completed. It is of interest to note that the gases weigh over five times as much as the pig iron, while the slag weighs about half as much as the pig iron.

The percentage compositions of the pig iron and the slag are obtained from the figures in the balance sheet, as follows:

Pig Iron

Fe = 993 = 91.0 per cent
Si = 26 = 2.4
Mn = 21 = 1.9
P = 7 = 0.6
C = 44 = 4.0

Slag

SiO_2 = 226 = 40.2 per cent
CaO = 227 = 40.4
MgO = 5 = 0.9
Al_2O_3 = 49 = 8.7
FeO = 13 = 2.3
MnO = 27 = 4.8
CaS = 16 = 2.8

The percentage composition of the gases should be calculated by volume. The total weight of carbon burned from the coke is 846,000 lb. The total weight of oxygen to combine with this is 1,500,000 lb. (obtained by adding all the oxygen items in the gases column). This will convert all the carbon to CO and some of this CO to CO_2.

846,000 × $\frac{16}{12}$ = 1,128,000 lb. of oxygen required for CO, forming 1,974,000 lb. of CO and leaving 372,000 lb. of oxygen for CO → CO_2.

This will oxidize $\frac{28}{16}$ × 372,000 = 651,000 lb. of CO, forming 1,028,000 lb. of CO_2 and leaving 1,323,000 lb. of CO. Adding the CO_2 from the flux gives 1,218,000 lb. of CO_2 total.

Blast-furnace gas:

CO = 1,323,000 × $\frac{359}{28}$ = 16,960,000 cu. ft. = 23.0 per cent
CO_2 = 1,218,000 × $\frac{359}{44}$ = 9,940,000 = 13.5
H_2O = 159,000 × $\frac{359}{18}$ = 3,170,000 = 4.3
H = 8,000 × $\frac{359}{2}$ = 1,430,000 = 1.9
N = 3,302,000 × $\frac{359}{28}$ = 42,340,000 = 57.3
Total = 73,840,000 cu. ft. = 100.0 per cent

The thermal balance sheet of the iron blast furnace is taken up on page 169.

THE IRON CUPOLA

The cupola is a small blast furnace used to melt pig iron for the purpose of making iron castings in the foundry. In addition to pig iron the charge usually contains iron scrap and often a small amount of limestone as a flux, together with the necessary coke. The cupola differs from the iron blast furnace in that there is no reduction of ore; on the contrary, there is some unavoidable oxidation of certain elements in the charge, some Si being slagged as SiO_2, Mn as MnO, and Fe as FeO. There may or may not be some loss of carbon by oxidation to CO and CO_2, such loss being counterbalanced by absorption of carbon in the iron from the coke. The cupola uses much less coke than the blast furnace per ton of iron, and the gases usually contain considerably more CO_2 than CO.

In other respects the operation of the cupola is similar to that of the blast furnace, and no additional principles are needed for calculations.

Unlike the blast furnace, which operates continuously, the cupola is commonly run intermittently, a few hours each day when the molds are ready for pouring the molten iron.

Problems

107. An iron ore is reduced in a shaft furnace in accordance with the following equation:

$$Fe_2O_3 + 9CO = 2Fe + 3CO_2 + 6CO$$

The necessary carbon monoxide is obtained by the combustion of coke at the bottom of the furnace. The coke contains 90 per cent C, of which 4 per cent is absorbed by the reduced iron and 86 per cent is burned to CO, no CO_2 being formed in the combustion.

Required: 1. The volume of CO necessary to reduce 1 metric ton of iron as required by the equation.

2. The theoretical weight of coke required in reducing 1 metric ton of iron.

3. The volume of air used in burning this amount of coke

4. The volume and percentage composition of the gases formed in the combustion.

5. The volume and percentage composition of the gases resulting from the combustion plus the ensuing reduction.

6. The volume of air used per ton of coke, measured at 600°C and 1,800 mm. total pressure.

108. A blast furnace makes pig iron containing:

	Per Cent
C	3.6
Si	1.4
Fe	95.0

The ore was 80 per cent Fe_2O_3, 12 SiO_2, 8 Al_2O_3.

The coke (1 kg. per kilogram of pig iron) carried 10 per cent SiO_2, 90 C.

The flux (0.40 kg per kilogram of pig iron) was pure $CaCO_3$

The gas contained 28 per cent CO and 12 CO_2.

Required: Per ton of pig iron made:

1. The weight of ore used

2. The weight of slag made.

3. The volume of the blast-furnace gas

109. An iron blast furnace uses ore and makes pig iron of the following compositions:

	Ore, Per Cent		Pig Iron, Per Cent
Fe_2O_3	84	Fe	94.0
SiO_2	9	Si	2.2
Al_2O_3	3	C	3.8
H_2O	4		

The flux (50 lb. per 100 lb. of pig iron) is:

	Per Cent
$CaCO_3$	95
SiO_2	5

The coke (90 lb. per 100 lb. of pig iron) is:

	Per Cent
C	84
SiO_2	10
Al_2O_3	3
H_2O	3

The gases analyze (dry analysis):

	Per Cent
CO	27
CO_2	14
N_2	59

Assume no iron lost in the slag.

Required: 1. The weight of ore smelted, per short ton of pig iron.

2. The weight of slag, per ton of pig iron.

3. The volume of the blast-furnace gas (including moisture), per ton of pig iron.

4. The percentage of the carbon of the coke that is burned at the tuyères.

110. An iron blast furnace produces pig iron of the following composition:

	Per Cent
Fe	93.6
Si	2.1
C	3.6
Mn	0.7

The ore used analyzes as follows:

	Per Cent
Fe_2O_3	78
SiO_2	9
Al_2O_3	5
MnO	1
H_2O	7

Assume that all the Fe_2O_3 is reduced to Fe.

The coke is 90 per cent C and 10 per cent SiO_2, and 1 ton of coke is used per ton of pig iron made.

The flux is pure $CaCO_3$, and enough is used to make a slag of 45 per cent CaO.

Required: 1. The kilograms of ore used per ton of pig iron made.

2. The percentage of the total SiO_2 and of the MnO reduced in the furnace.

3. The weight of slag made per ton of pig iron, and its percentage composition.

111. The ore used in an iron blast furnace was of the following composition:

	Per Cent
Fe_2O_3	82
SiO_2	14
Al_2O_3	2
H_2O	2

0.22 lb. of $CaCO_3$ was charged for every pound of ore. The coke amounted to 1 lb. per pound of pig made and was 90 per cent C and 10 per cent ash. The furnace produced per day 600 long tons of pig iron, which was 94 per cent Fe, 4 C, 2 Si.

The blast-furnace gas analysis showed the proportion of CO to CO_2 to be 3:2. Assume the blast dry.

Required: 1. The weight of ore charged per day.

2. The volume of gas produced per ton of pig iron.

3. The volume and weight of the blast per ton of pig iron.

4. The weight of carbon burned at the tuyères per ton of pig iron (see also Prob. 177).

112. An iron ore has the following composition:

	Per Cent
Fe_2O_3	76
SiO_2	14
MnO	1
Al_2O_3	9

It is smelted in a blast furnace, producing pig iron of the following analysis:

	Per Cent
Fe	94.2
C	3.5
Si	1.5
Mn	0.8

Per ton of pig iron, there is used 1,100 kg. of coke containing 88 per cent C and 12 per cent SiO_2.

The gases analyze 26 per cent CO, 13 CO_2, 61 N_2.

Assume no iron lost in the slag.

Required. 1. The weight of ore necessary to yield 1 ton of pig iron.

2. The weight of limestone (pure $CaCO_3$), per ton of pig iron, required to give a slag containing 36 per cent CaO.

3. The volume of the gases, per ton of pig iron.

4. The volume of the blast, calculated both on the oxygen and on the nitrogen basis.

113. The ore smelted in an iron blast furnace contained the following:

	Per Cent		Per Cent
Fe_2O_3	75.4	Al_2O_3	4.0
MnO	2.6	P_2O_5	1.1
SiO_2	11.0	H_2O	5.9

The coke composition was 88 per cent C, 8 SiO_2, 2 FeS, 2 H_2O. The flux was 96 per cent $CaCO_3$ and 4 SiO_2. The amount of the coke used was 910 kg. per ton of pig iron, and the flux was 330 kg. per ton of pig iron.

The pig iron produced analyzed:

	Per Cent		Per Cent
C	3.8	P	0.7
Si	1.2	S	0.2
Mn	0.9	Fe	93.2

99 per cent of the iron in Fe_2O_3 was reduced, 1 per cent slagged. Sulphur not in the pig iron enters the slag as CaS.

The gases contained $1\frac{3}{4}$ parts CO to 1 part CO_2 by volume.

Required: 1. The weight of ore required per 1,000 kg. of pig iron.

2. The weight of slag made.

3. The percentage of the SiO_2, the MnO, and the P_2O_5 which were reduced in the furnace.

4. The volume of the blast-furnace gas, per 1,000 kg. of pig iron.

5. The number of kilowatt-hours of energy represented by the calorific power of the gas, per 1,000 kg. of pig iron (at 100 per cent conversion).

114. A blast furnace uses ore of the following composition:

	Per Cent
Fe_2O_3	90
SiO_2	10

The coke was 90 per cent C and 10 per cent ash (SiO_2). The flux was limestone containing 95 per cent $CaCO_3$, 3 per cent $MgCO_3$, and 2 per cent SiO_2.

1 ton of coke is used per ton of pig iron produced.

The pig iron produced contains C, 4.0 per cent; Si, 1.0.

The gases produced contain CO_2, 12 per cent; CO, 24; H_2, 2; CH_4, 2; N_2, 60 (dry analysis).

The slag must contain 45 per cent CaO + MgO; assume no FeO in the slag.

Required. 1. The weight of limestone necessary.

2. The amount of gases produced per 100 kg. of pig iron.

3. The volume of blast (considered dry) per 100 kg. of pig iron.

4. The percentages of the carbon of the coke oxidized at the tuyères and above the tuyères.

115. An iron blast furnace makes pig iron of the following composition:

	Per Cent
C	4.0
Si	1.2
Mn	0.9
Fe	93.9

The ore smelted carries Fe_2O_3, 80 per cent; MnO, 1; SiO_2, 12; Al_2O_3, 3; H_2O, 4. Per ton of pig iron made, there is used 1,750 kg. of ore; some iron is lost in the slag as FeO.

The volume of gas produced is 4,200 cu. m. per ton of pig iron, and its composition is CO, 26 per cent; CO_2, 12; H_2O, 4; N_2, 58.

The coke is 90 per cent C and 10 SiO_2. The flux, 480 kg. per ton of pig iron, is pure $CaCO_3$.

Required: 1. The kilograms of coke used per ton of pig iron.

2. The percentage composition of the slag.

3. The volume of the blast per ton of pig iron.

4. The carbon burned by the blast (all goes to CO), and the volume of CO formed from it.

5. The volume of this CO changed to CO_2 in passing through the furnace, and the percentage of the total CO_2 in the gas which is formed in this way.

116. An iron blast furnace produces pig iron of the following composition:

	Per Cent
Fe	93.6
Si	2.1
C	3.6
Mn	0.7

Per ton of pig iron made, there is charged 1,740 kg. of ore of the following composition:

	Per Cent
Fe_2O_3	78
SiO_2	9
Al_2O_3	5
MnO	1
H_2O	7

Some iron is unreduced, entering the slag as FeO.

The coke is 90 per cent C and 10 per cent SiO_2; 1 ton is used per ton of pig iron made. The flux is pure $CaCO_3$ and 360 kg. is used per ton of pig iron made.

Five-eighths of the carbon that oxidizes in the furnace goes to CO, three-eighths to CO_2.

Required: 1. The kilograms of slag made per ton of pig iron.

2. The cubic meters of blast used per ton of pig iron.

3. The cubic meters of gas made per ton of pig iron, and its percentage composition.

117. The ore used in an iron blast furnace was of the following composition:

	Per Cent
Fe_2O_3	85
SiO_2	11
Al_2O_3	4

For every 1.7 kg. of ore there were charged 1 kg. of coke (90 per cent carbon and 10 per cent ash) and 0.25 kg. of limestone (assume pure $CaCO_3$). The furnace produced per day 500 tons of pig iron containing 94 per cent Fe, 4 C, and 2 Si.

The volume of the blast was 3,150 cu. m. per ton of pig iron.

Required: 1. The weight of ore charged per day.

2. The ratio of CO to CO_2 in the blast-furnace gas, by volume.

3. The percentage of the total heating value of the coke left available in the gas.

4. The percentage of the carbon of the coke that was burned at the tuyères.

118. Iron ore of the following composition was smelted in a blast furnace.

	Per Cent
Fe_2O_3	82
SiO_2	10
Al_2O_3	5
H_2O	3

The flux used was $CaCO_3$ (assumed pure), and the coke was 88 per cent C, 1 H, and 11 SiO_2.

Per ton of ore smelted, there were used 600 kg. of coke, 120 kg. of flux, and 2,140 cu. m. of blast, and there was produced 590 kg. of pig iron analyzing 95 per cent Fe, 3.5 C, 1.5 Si.

Required: 1. The weight of slag made per ton of ore, and its percentage composition.

2. The volume of the blast-furnace gas, and its percentage composition.

3. The weight of blast used per ton of pig iron made, and its volume measured under the conditions used, *viz.*, temperature, 600°C.; pressure, 2,000 mm. of mercury.

119. The following iron ore was smelted in a blast furnace using 3,400 lb. of ore per short ton of pig iron made.

	Per Cent
Fe_2O_3	80
MnO	3
SiO_2	10
Al_2O_3	3
H_2O	4

The flux was pure $CaCO_3$ and the coke was 87 per cent C, 11 SiO_2, 2 Al_2O_3. The coke consumption was 1,700 lb. per ton of pig iron, and enough flux was used to make a slag of 34.6 per cent CaO.

The blast was 91,000 cu. ft. per ton of pig iron.

The pig iron contained 93 per cent Fe, 2 Mn, 1.4 Si, 3.6 C.

Required: 1. The pounds of flux used per ton of ore.

2. The percentage composition of the slag.

3. The cubic feet of gas per ton of pig iron, and its percentage composition

4. The percentage of the heating value of the coke that remains in the gas

120. A hematite iron ore contains 78 per cent Fe_2O_3 It is reduced in a blast furnace using coke carrying 83 per cent C. The furnace gas must contain an excess of CO, the reduction equation having the form

$$Fe_2O_3 + xCO = 2Fe + 3CO_2 + yCO.$$

Assume that the ratio of $CO:CO_2$ in the gas made is 7.4

The pig iron produced contains 93 per cent Fe and 4 per cent C.

Required: 1. The reduction equation, balanced with whole numbers.

2. The coke consumption per metric ton of pig iron.

3 The CO for reduction is made by burning the carbon of the coke with air (blast). How many cubic meters of blast are required per ton of pig iron made? How many tons of blast?

4. What will be the percentage composition of the gas resulting from the combined combustion and reduction?

121. The equation for the reduction of Fe_2O_3 by CO is as follows:

$$Fe_2O_3 + xCO = 2Fe + 3CO_2 + yCO. \qquad (1)$$

The pig iron carries 94 per cent Fe and 3.6 per cent C. The carbon is supplied by coke carrying 84 per cent C.

Required: 1. The equation for the reduction producing a $CO:CO_2$ ratio of 2:1

2. The coke consumption in pounds per long ton of pig iron produced.

3. If the CO for reduction is produced by burning the carbon of the coke by air, how many cubic feet of air would be required to produce the CO necessary for 1 ton of pig iron?

4. What will be the percentage composition of the gas mixture resulting from the combined combustion and reduction?

5. If the ore used carried 75 per cent Fe_2O_3, how many tons of ore will be used per ton of pig iron made?

6. If, in combination with Eq. (1), 10 per cent of the iron were reduced by solid carbon according to the equation

$$Fe_2O_3 + 3C = 2Fe + 3CO,$$

what would be the coke consumption per ton of pig iron, assuming the same ratio of 2:1 for the $CO:CO_2$ in the gases?

122. An iron blast furnace smelts per day 1,000 tons of ore containing:

	Per Cent
Fe_2O_3	80
SiO_2	12
MnO_2	5
Al_2O_3	2
H_2O	1

All the Fe_2O_3, one-half the MnO_2, and one-fourth the SiO_2 are reduced in the furnace. The pig iron carries 4 per cent C 0.2 lb. of $CaCO_3$ is used per pound of ore, and 0.5 lb. of coke per pound of ore, the coke being 90 per cent C and 10 per cent SiO_2. Assume SiO_2 of the coke to be entirely slagged The furnace gases contain 24 per cent CO and 9 per cent CO_2. Manganese in the slag exists as MnO.

Required: 1. The pounds of pig iron made per day

2. The pounds of slag made per day.

3. The cubic feet of gases made per day.

123. An iron blast furnace smelts ore of the following composition:

	Per Cent		Per Cent
Fe_3O_4	70	P_2O_5	1
Fe_2O_3	5	MnO_2	4
SiO_2	10	H_2O	10

It produces per day 900 metric tons of pig iron Enough flux is used to give a slag containing 24 per cent CaO. The flux is pure limestone. 0.48 ton of coke is used per ton of ore. The coke is 86 per cent C, 9 SiO_2, 5 H_2O All the P charged, one-half the Mn, and one-fifth the Si are reduced and go in the pig iron, which also contains by analysis 4 per cent C. 88 per cent of the carbon of the coke is burned at the tuyères. Assume no iron in the slag.

Required: 1. The percentage composition of the pig iron.

2. The weight of ore smelted per day.

3. The weight of flux used per day.

4. The percentage composition of the flue gases.

124. An iron blast furnace smelts the following ore:

	Per Cent		Per Cent
Fe_2O_3	77	SiO_2	11
MnO	3	Al_2O_3	4
P_2O_5	3	H_2O	2

The coke is 90 per cent C, 9 SiO_2, and 1 H_2O 1,200 lb of coke is used per ton of ore

The flux (100 per cent $CaCO_3$) amounts to 860 lb. per ton of pig iron made.

The blast-furnace gas carries 2½ parts of CO to 1 part of CO_2.

The furnace reduces to metal all of the Fe_2O_3, nine-tenths of the MnO, all of the P_2O_5, and one-fifth of all the SiO_2.

The pig iron is 4 per cent C.

Required: 1. The pounds of pig iron made from 1 ton of ore.

2. The pounds of slag made, per ton of pig iron.

3. The cubic feet of blast used, per ton of pig iron.

4. The cubic feet of gas made, per ton of pig iron.

125. A blast furnace smelts 1,400 metric tons per day of the following ore:

	Per Cent		Per Cent
Fe_3O_4	68	$Ca_3(PO_4)_2$	3
Fe_2O_3	8	SiO_2	12
MnO	5	H_2O	4

Enough flux (pure $CaCO_3$) is used to make a slag of 38 per cent CaO. 0 7 ton of coke is used per ton of ore; the coke is 88 per cent C, 8 SiO_2, 4 H_2O.

The blast is 4,000 cu. m. per ton of pig iron.

The following amounts are reduced: Fe and P, 100 per cent; Mn, 40; Si, 22 The Fe absorbs 4 per cent of its weight of carbon.

Required: The weight and percentage composition of the pig iron and slag; and the volume and percentage composition of the blast-furnace gas, per day

126. An iron blast furnace smelts ore carrying 75 per cent Fe_2O_3 and 5 per cent H_2O, making pig iron containing 4 per cent C and 92 per cent Fe. It uses 1 ton of coke for each ton of pig iron produced, the coke being 90 per cent C and 1 per cent H_2O, and 260 kg. of $CaCO_3$ for each ton of pig iron. The volume of the blast is 3,250 cu. m. per ton of pig iron.

Assume that the iron is all reduced, and neglect reduction of Si and other elements

Required: 1. The weight of ore used to make 1 ton of pig iron.

2. The percentage of the carbon of the coke that is burned at the tuyères and above the tuyères.

3. The volume and percentage composition of the gas formed at the tuyères, per ton of pig iron.

4. The volume and percentage composition of the blast-furnace gas.

5. The percentage of the calorific power of the coke that is developed in the furnace.

127. A blast furnace uses coke of the following composition.

	Per Cent
C	84
H	2
O	1
H_2O	3
Ash	10

The furnace makes 1 ton (1,000 kg.) of pig iron for each ton of coke used and also uses 400 kg. of $CaCO_3$ in the charge, per ton of pig iron made. The pig iron is 4 per cent C.

The gas issuing from the furnace analyzes:

	Per Cent
CO	28
CO_2	16
CH_4	1
H_2	1
N_2	54

Required: 1. The cubic meters of gas made, per ton of pig iron.

2. The calorific power of the coke, per kilogram.

3. The percentage of the calorific power of the coke available in the gas.

128. A blast furnace uses 2,940 cu. m. of blast per ton of pig iron produced, preheating this blast to 560°C. in stoves having a thermal efficiency of 70 per cent. To do this requires 28 per cent of the gas produced by the blast furnace, this gas consisting of CO, CO_2, and N_2 and containing 1.9 parts CO to 1 part CO_2.

The charge includes 320 kg. of $CaCO_3$ per ton of pig iron produced. The pig is 4 per cent C. The coke used is 86 per cent C.

Required: 1. The volume of the blast-furnace gas, per ton of pig iron, and its percentage composition.

2. The kilograms of coke used, per ton of pig iron.

3. Of the carbon in the coke, what percentage:

a. Issues from the furnace as CO?

b. Is used in the stoves as CO?

c. Is available as CO for power generation?

d. Is burned at the tuyères?

129. An iron blast furnace makes 400 short tons of pig iron per day, of the following composition:

	Per Cent
Fe	92.8
Si	2.1
C	3.8
Mn	1.3

The ore used analyzes:

	Per Cent
Fe_2O_3	78.0
SiO_2	8.2
Al_2O_3	4.2
MnO	4.5
H_2O	5.1

The flux, pure $CaCO_3$, amounts to one-fourth the ore. 5 per cent of the iron charged is lost in the slag. The coke is 92 per cent C, and 2,100 lb. is used per ton of pig. The gases (dry) contain 12 per cent CO_2, 28 CO, 60 N_2. The blast is preheated to 700°C., in stoves having an efficiency of 70 per cent.

Required: 1. The weight of ore used, per ton of pig iron.

2. The volume of the gas (dry), per ton of pig iron.

3. The percentage of the heating value of the coke that remains in the gas.

4. The percentage of the gas required by the stoves.

5. The power that can be generated from the remainder of the gas at 20 per cent conversion efficiency.

130. Pig iron of the following composition was made in a blast furnace:

	Per Cent
C	3.9
Mn	1.1
Si	2.1
Fe	92.9

The ore smelted contained:

	Per Cent
Fe_2O_3	82
SiO_2	8
MnO	4
Al_2O_3	4
H_2O	2

Enough $CaCO_3$ was used to make a slag of 40 per cent CaO.

The coke was 88 per cent C, 8 SiO_2, 1 Al_2O_3, 3 H_2O and amounted to 950 kg. per ton of pig iron.

The gases carried 29 per cent CO, 13 CO_2, 58 N_2 (dry analysis).

The blast was preheated to 800°C. in stoves having an efficiency of 72 per cent. The gas not required by the stoves was used to generate power in gas engines at an efficiency of 25 per cent.

Required: 1. The kilograms of ore smelted, per ton of pig iron made, neglecting loss of iron in the slag.

2. The kilograms of slag made, and the kilograms of $CaCO_3$ needed.
3. The cubic meters of blast-furnace gas (including the H_2O).
4. The cubic meters of blast (assumed dry).
5. The proportion of the gas required by the stoves.
6. The power generated from the remainder of the gas, if the furnace makes 1,000 tons of pig iron per day.

131. The gas produced in an iron blast furnace amounted, per 1,000 kg. of pig iron, to 4,200 cu. m., the analysis being as follows:

	Per Cent
CO	28 7
CO_2	10.3
H_2	0.5
N_2	59 0
H_2O	1 5

The furnace makes 528 tons of pig iron containing 4 per cent C per day, using 70 tons of limestone ($CaCO_3$)

The coke used is 85 per cent C

The blast is preheated to a temperature of 700°C in stoves having a thermal efficiency of 65 per cent.

The gas not used in the stoves is used in gas engines operating at a net efficiency of 22 per cent.

Required: 1. The cubic meters of blast used, per ton of pig iron

2. The kilograms of coke used, per ton of pig iron.
3. The percentage of the carbon of the coke that is burned at the tuyères.
4. The calorific power of the gas, per cubic meter.
5. The percentage of the total gas used in the stoves
6. The power generated by the gas engines.

132. Calculate the theoretical temperature in the smelting zone of an iron blast furnace, under three hypothetical conditions, as follows:

1. The blast not heated (assume 0°C.).
2. The blast heated to 700°C.
3. The blast being oxygen-enriched air containing 30 per cent O_2, not heated.

In each case assume that the coke is preheated by the ascending hot gases to the theoretical temperature of combustion, before it burns.

Neglect moisture in the blast.

133. An iron blast furnace uses 3,250 cu. m. of blast per ton of pig iron The blast is preheated to 600°C. in stoves having a thermal efficiency of 60 per cent. The furnace makes 500 tons of pig iron per day.

The blast-furnace gas that is not needed by the stoves is used for power production, one-half being burned under boilers at a thermal efficiency of 70 per cent, and one-half being used directly in gas engines at an efficiency of 25 per cent. The composition of the blast-furnace gas is:

	Per Cent
CO	24.5
CO_2	13.4
H_2O	2.8
N_2	59.3

Assume that the carbon of the coke is preheated to the temperature at the tuyères before burning.

Required: 1. The percentage of the total gas that is used in the stoves.

2. The boiler horsepower developed in the boilers.

3. The mechanical horsepower developed by the gas engines.

4. The maximum theoretical temperature at the tuyères.

134. A blast furnace uses blast preheated to 600°C. In wet weather the air contains 5 per cent water vapor This is decomposed on entering the furnace according to the reaction

$$H_2O + C = CO + H_2.$$

Assume that the burning carbon in the tuyère zone is at the maximum temperature of the gases.

Required: 1 The theoretical maximum temperature of the gases in the tuyère zone when the blast is dry.

2 The same, when the blast contains 5 per cent H_2O.

3. The ratio of change in smelting power in the two cases

135. An iron blast furnace uses blast that at the entrance to the stoves has a pressure of 1 6 atm. gage and a temperature of 45°C and is saturated with water vapor. The stoves heat it to 700°C.

Assume that the carbon of the coke just before it is consumed by the blast has reached a temperature 300°C. less than the temperature of the hot gases resulting from the combustion

Required: 1. The theoretical maximum temperature in the smelting zone of the furnace.

2 The temperature if the blast were dried completely

3. The temperature if the blast were neither dried nor preheated, entering the furnace at 0°C.

136. The following data were taken from a blast furnace making 600 tons of pig iron daily:

Ore used, per cent		Coke used, per cent		Flux used, per cent		Gas made, per cent		Pig made, per cent	
Fe_2O_3	90	C	86	SiO_2	5	CO	24	Si	1 4
SiO_2	5	SiO_2	6	$CaCO_3$	75	CO_2	12	C	3 6
Al_2O_3	3	Al_2O_3	5	$MgCO_3$	20	H_2	2	Fe	95
CaO	1	CaO	1			CH_4	2		
H_2O	1	MgO	1			N_2	60		
		H	1						

The slag made carries 45 per cent CaO + MgO. 0.9 ton of coke is used per ton of pig iron made. After supplying the stoves, the remainder of the gas, used in gas engines at 25 per cent thermomechanical efficiency, generated 17,340 kw. The blast temperature was 700°C.; pressure, 1.3 atm. gage.

Assume the specific heat of the coke the same as for pure C. Assume that the free H_2 and H_2 in CH_4 in the gas are derived from H in the coke and decomposition of H_2O in the blast by carbon.

Required: 1. The weight of ore used, per ton of pig iron.

2. The weight of flux used, per ton of pig iron.

3. The weight of slag used, per ton of pig iron.

4. The volume of gas made, per ton of pig iron (dry)

5. The volume of blast used, per ton of pig iron (including moisture).

6. The thermal efficiency of the stoves.

7. The partial pressure of the water vapor in the blast, and the number of gallons of water entering the furnace per minute in the blast.

8. The percentage of the heat generated by the combustion of carbon at the tuyères that is absorbed by the decomposition of H_2O.

9. The saving in tons of coke daily by removing 70 per cent of this water vapor

10. The lowering of the temperature at the tuyères caused by water vapor.

137. A blast furnace runs under two atmospheric conditions:

a. Blast dry, barometer 760 mm., temperature 600°C.

b. Blast moist, barometer 700 mm., temperature 600°C., saturated with moisture at 25°C. before heating.

The engines run at constant speed or constant piston displacement.

The critical temperature needed in the smelting zone is assumed to be 1500°C. Assume the carbon burned in the smelting zone to be preheated to this temperature.

Required: 1. The maximum theoretical temperature of the gases in the smelting zone, in case *a.*

2. The same, in case *b.*

3. The relative weights of carbon burned per day in the region of the tuyères by the blast, in the two cases.

4. If, in case *a*, 800 kg. of carbon is needed before the tuyères per ton of pig iron produced, how much would be required in case *b*?

138. The slag and the pig iron in a blast furnace are raised in the smelting zone to 1500°C. The blast enters the furnace at 700°C. The outside air is at 28°C., and is one-half saturated with moisture. Barometer, 735 mm.

Assume the carbon just before burning to be at the temperature of 1500°C.

Required: 1. The maximum theoretical temperature of the hot gases before the tuyères.

2. The maximum temperature, if the blast were enriched to 28 per cent oxygen.

3. Compare in the two cases the relative smelting power of the furnace.

139. The following ore was smelted in an iron blast furnace:

	Per Cent		Per Cent
Fe_2O_3	78 0	MnO	2 6
SiO_2	8 2	P_2O_5	1 9
Al_2O_3	4 0	H_2O	5.3

The coke used analyzed C, 88 per cent; SiO_2, 10; H_2O, 2. The flux was pure $CaCO_3$.

The coke amounted to three-fifths the weight of the ore, and the flux to one-fourth the weight of the ore.

The furnace reduced all the phosphorus, one-half the manganese, and one-fifth the silica charged. Assume that no iron was lost in the slag, but the iron absorbed carbon amounting to 4 per cent of its weight.

The blast was 1,500 cu m. per ton of ore (assumed dry).

Required: 1. A balance sheet of the furnace, based on 1,000 kg. of ore.

2. The percentage composition of the pig iron, slag, and gas.

140. A blast furnace smelts 900 short tons of iron ore per day, using ⅙ kg. of $CaCO_3$ per kilogram of ore and 0.6 kg. of coke per kilogram of ore, the coke being 85 per cent C and 15 SiO_2. The ore analyzes as follows:

	Per Cent		Per Cent
Fe_2O_3	80	P_2O_5	1
SiO_2	9	Al_2O_3	6
MnO	2	H_2O	2

The furnace reduces to metal all of the Fe_2O_3 and P_2O_5 charged, also three-fourths of the MnO and one-fifth of all the SiO_2. The pig iron analyzes 4 per cent C

The furnace gases contain 26 per cent CO and 11 per cent CO_2

Required: 1. A complete charge balance of the furnace, based on pounds per day.

2. The percentage composition of the slag and gases

141. An iron blast furnace produces pig iron of the following composition:

	Per Cent		Per Cent
Fe	92.8	P	0.9
Si	2.1	Mn	0.3
C	3.8	S	0.1

The ore used analyzes as follows:

	Per Cent		Per Cent
Fe_2O_3	78.0	P_2O_5	1.9
SiO_2	8.2	MgO	1.2
Al_2O_3	3.0	H_2O	5.1
MnO	2.6		

The flux used amounts to one-fourth the weight of the ore and is composed of:

	Per Cent
$CaCO_3$	96
$MgCO_3$	2
SiO_2	2

The coke is 1,000 kg per ton of pig iron and contains the following

	Per Cent
C	88
SiO_2	8
FeS	2
H_2O	2

The gases contain 2⅓ parts of CO to 1 part of CO_2

Assume the Fe of the ore all reduced, Fe of the coke all slagged S not in pig iron goes in the slag as CaS. P not in pig iron goes in the slag as P_2O_5

Required. 1 The weight of ore used, per ton of pig iron

2. A complete balance sheet of the furnace, per ton of pig iron.

3. The percentage composition of the slag and of the gases

142. An iron blast furnace produces pig iron of the following composition

	Per Cent
Fe	93.4
Si	2.3
C	3.8
Mn	0.5

The ore smelted analyzes as follows.

	Per Cent
Fe_2O_3	80.0
SiO_2	8.3
Al_2O_3	3.5
MnO_2	3.1
H_2O	5.1

The flux amounts to one-fourth the weight of the ore and contains 96 per cent $CaCO_3$ and 4 per cent SiO_2. The coke amounts to 1,900 lb. per ton of pig iron and carries C, 88 per cent; SiO_2, 8; H_2O, 4.

The blast is 95,000 cu. ft. of air per ton of pig iron. Assume that all the iron is reduced.

Required: 1. The weight of ore used, per ton of pig iron.

2. A complete balance sheet of the furnace.

3. The volume of the blast-furnace gas.

143. The ore smelted in an iron blast furnace contains the following:

	Per Cent		Per Cent
Fe_2O_3	76	P_2O_5	1
MnO_2	3	H_2O	4
SiO_2	11	CaO	2
Al_2O_3	3		

The coke has this composition:

	Per Cent
C	86
SiO_2	9
Al_2O_3	1
FeS	2
H_2O	2

The limestone carries:

	Per Cent
CaO	50
MgO	5
Al_2O_3	1
SiO_2	1
CO_2	13

The pig iron analyzes:

	Per Cent		Per Cent
C	3.8	P	0.75
Si	0.9	Fe	93.4
Mn	1.05	S	0.1

1 ton of coke is used per ton of pig iron made. Assume that 2 per cent of the Fe charged is lost in the slag as FeO. The slag contains equal parts of CaO and SiO_2.

82 per cent of the carbon in the coke is burned at the tuyères

Sulphur not in the pig iron enters the slag as CaS.

Manganese not in the pig iron enters the slag as MnO.

Required: 1. A complete charge balance of the furnace (based on 1,000 kg of pig iron).

2. The percentage composition of the slag and gases

144. The electric pig-iron furnaces at Domnarfvet, Sweden, smelt the following ore:

	Per Cent		Per Cent
Fe_3O_4	65.0	CaO	5.8
Fe_2O_3	20.6	SiO_2	5.3
MnO	0.9	P_2O_5	2.4

The pig iron made contains:

	Per Cent
C	3.8
Si	0.5
Mn	0.8
P	1.6
Fe	93.3

There are used per metric ton of pig iron made 1,520 kg. of ore, 60 kg of $CaCO_3$, 320 kg of charcoal (assume pure carbon). Electrode consumption, 8 kg (assume pure carbon). No blast is used, but 250 cu. m. of air per ton of pig iron leaks in at the bottom of the furnace.

Required: 1. The amount of slag, per ton of pig iron.

2. The percentage reduction of the iron, phosphorus, manganese, and silica

3. The percentage composition of the gas.

4. The percentage of the heating value of the charcoal available in the gas

5. The kilowatts that can be obtained by using the gas in gas engines at 25 per cent efficiency, assuming that the furnace produces 30 tons of pig iron per day.

145. A cupola used for making iron castings is charged with pig iron, flux, and coke The flux is pure $CaCO_3$, and 25 kg is used per ton of pig iron charged The coke is 86 per cent C, 5 SiO_2, 7 Al_2O_3, 2 FeO, and 120 kg is used per ton of pig iron.

The gas from the cupola contains equal parts of CO and CO_2 by volume. No carbon is oxidized from the pig iron

The slag from the cupola carries:

	Per Cent
FeO	11
SiO_2	46
MnO	3
CaO	25
Al_2O_3	15

The cast iron produced carries 3.8 per cent carbon, besides some manganese and silicon.

Required Per ton of pig iron charged:

1. The weight of the slag
2. The volume of air consumed in oxidizing silicon, manganese, and iron.
3. The volume of air consumed in oxidizing the carbon of the coke.
4. The volume and percentage composition of the gas.

146. The pig iron melted in a cupola had the following composition:

	Per Cent		Per Cent
Fe	91.0	Mn	0.7
C	3.6	P	0.7
Si	2.0	Dirt	2.0

The dirt on the pig consisted of sand and clay and analyzed 75 per cent SiO_2 and 25 per cent Al_2O_3. The temperature of the melted iron was 1300°C. and its melting point was 1180°C.

25 kg. of limestone was used per ton of pig, analyzing $CaCO_3$, 98 per cent; SiO_2, 1; Al_2O_3, 1. The weight of coke used was 125 kg per ton of pig, and it analyzed C, 90 per cent; SiO_2, 5; Al_2O_3, 3; FeO, 2.

Gas Made, Per Cent	
CO_2	14
CO	10
N_2	76

Slag Made, Per Cent	
FeO	11
SiO_2	46
MnO	3
CaO	25
Al_2O_3	15

The temperature of the gas leaving the cupola was 440°C.

Required: 1 The cubic meters of gas made and of blast used, per ton of pig melted.

2. The percentage of the Fe, Mn, and Si of the pig that was oxidized during melting.

3. The weight of cast iron produced.

4. The percentage of the calorific power of the coke represented by the heat in the melted cast iron. (For heat content, see page 395.)

5. The percentage of the calorific power of the coke lost in the gases (*a*) in the sensible heat; (*b*) by imperfect combustion.

147. A cupola melts per hour 15 short tons of foundry iron containing 3.5 per cent C, 2.2 Si, 0.8 Mn, 0.7 P and 5 tons of scrap containing 3.0 per cent C, 1.8 Si, 1.1 Mn, 0.2 P.

The blast is computed on the basis of 30,000 cu. ft measured at 40°C required to melt 1 ton of iron and scrap charge per minute. Assume the blast to be dry.

In melting there is oxidized 20 per cent of the Si in the iron and scrap charged, 15 per cent of the Mn, 1 per cent of the Fe, and no P; 5 per cent of the carbon is also oxidized, but 1 per cent of the carbon in the coke is absorbed by the iron in melting. Enough $CaCO_3$ is charged to give a slag of 30 per cent CaO. The coke is 92 per cent C and 8 per cent SiO_2, and the ratio of weight of coke to weight of pig and scrap charged is 1:9.

Required: 1 A charge balance of the cupola for a 5-hr run.

2. The percentage composition of the resulting cast iron, slag, and gases

CHAPTER VII

THE BESSEMER, OPEN-HEARTH, AND ELECTRIC STEEL PROCESSES

The Bessemer and open-hearth processes for the production of steel consist essentially in purification of pig iron through oxidation of the impurities in it. Besides pig iron a large amount of iron and steel scrap is charged in the open-hearth furnace; and although this may not contain impurities in excess of the amounts that will be present in the finished steel, it undergoes the same oxidizing reactions as the pig iron, with which it mixes in the molten state. A small amount of scrap may also be charged in the Bessemer converter.

Although carbon is desired in a definite amount in the finished bath, it is unavoidable that much of the carbon in the charge will be oxidized during oxidation of the other elements. In order to adjust the carbon content of the bath accurately and to avoid complications of procedure, it is customary to oxidize most of the carbon—often all of it, especially in the Bessemer process—and then to recarburize to the desired percentage as the final step. Unavoidably, a small amount of the iron will also be oxidized, leaving some iron oxide in the bath, which must, so far as possible, be reduced to iron, before the molten steel is cast into ingots. The deoxidation and recarburization are accomplished simultaneously. Calculations can often be based on the assumption of complete removal of the carbon as well as the other oxidizable impurities, prior to recarburization. Allowance should be made for oxidation of iron.

The oxidation of impurities from pig iron to make steel is chemically the reverse of the action of reduction in the blast furnace and is governed by similar simple equations, involving, however, combination with, instead of removal of, oxygen. Calculation of air and flux requirements and of the amounts and compositions of the slag and gases formed can be carried out.

This chapter will deal principally with charge and product calculations of the kind just indicated for the production of steel by the three processes that account for virtually all the steel made. Although the Bessemer process currently is used for only about 7 per cent of the steel made in the United States, it will probably increase somewhat in importance rather than lose further ground because of recent improvements in control. It is the earliest of the three methods and at one time was the principal steelmaking process. Here it will be taken up first because it is chemically the simplest and involves the simplest types of calculation.

THE BESSEMER STEEL PROCESS

In this process the pig iron is poured molten into the converter, and a strong blast of air is sent up through it. No fuel is used. The blast is not preheated. In usual practice virtually all the impurities are oxidized, leaving nearly pure iron save for some dissolved oxygen. It is scarcely practicable to consider the dissolved oxygen in ordinary calculations, nor is the ensuing step of deoxidation and recarburization one which lends itself readily to useful computations. The amount of scrap charged in the Bessemer process is minor compared with the molten pig iron, and it may be disregarded in typical problems.

The carbon is oxidized partly to CO and partly to CO_2, these, together with the nitrogen of the blast and a little hydrogen from moisture in the blast, constituting the gases which go out at the mouth of the converter. There is no oxygen in them, as all the oxygen of the air is consumed in oxidation. In the early part of the blow, the ratio of CO to CO_2 in the gases is low; but as the temperature rises, the ratio grows larger, and toward the end fully 90 per cent of the carbon is going to CO. On the average for the blow, about three-fourths of the carbon forms CO.

The silicon is oxidized to SiO_2, the manganese to MnO. There is also some oxidation of iron (to FeO), in accordance with the principles of mass action, so much more iron being present than any other element. In general the impurities oxidize in the order of their affinities for oxygen, and FeO formed is always subject to being reduced again so long as any of the chemically stronger impurities remain; *e.g.*:

$$FeO + Mn = MnO + Fe.$$

But the FeO may also combine with the SiO_2 to form slag, and analyses of converter slags show that considerable iron is slagged even in the early stages of the blow; the amount of iron so lost often grows much larger toward the end of the blow, since the already predominant element Fe increases relatively as the impurities are removed.

In American practice no flux is used. An acid slag results, and phosphorus, whose affinity for oxygen is materially lessened at the high temperature prevailing, either does not oxidize or does not remain oxidized because it is not taken up by the slag. Acid Bessemer practice is therefore limited to pig irons relatively low in phosphorus. In European practice pig iron high in phosphorus is sometimes treated by the Thomas, or basic, process, in which CaO is added to the converter as a flux, forming a strongly basic slag which takes up the phosphorus as calcium phosphate. The amount of sulphur in the bath remains practically unchanged in either acid or basic practice.

The acid Bessemer blow may be divided into two periods, the first including the oxidation of the silicon and manganese, which have relatively strong affinities for oxygen, and the second the oxidation of the carbon. In practice there is some overlapping between the periods, but the division is fairly distinct and is evidenced by the appearance of the flame issuing from the mouth of the converter.

At the end of the blow, before recarburization, the percentage of each of the elements carbon, manganese, and silicon in the bath has normally been reduced to less than 0.1 per cent, although the practice is sometimes varied in such a way as to leave larger percentages. In calculations it is customary to assume complete elimination of impurities unless there is information to the contrary. In basic practice the phosphorus also is reduced below 0.1 per cent. This oxidation takes place in a third period following the removal of carbon, since at high temperatures phosphorus is oxidized less readily than carbon.

In view of the theory stated above with regard to the oxidation of iron—which is borne out in practice by analyses of Bessemer slags at different stages of the blow—it seems best to assume in most calculations that the oxidation of iron proceeds at *a uniform rate* throughout the blow in the acid Bessemer; in the basic Bessemer it might be assumed that some iron (say one-third) is oxidized in the second period, the rest in the third; or it might be assumed that iron is oxidized at a uniform rate just as in the acid process. The total amount of iron in the slag at the end varies from about 10 to 20 per cent of the slag. Most of this is present as FeO, though some is in the form of pellets of metallic iron.

Example 13

An acid Bessemer converter blows 20 metric tons of the following pig iron:

	Per Cent
C	4.0
Mn	1.2
Si	1.4
Fe	93.4

Besides the impurities there is oxidized iron equivalent to 1.5 per cent of the pig, assume the iron oxidized at a uniform rate. Three-fourths of the carbon goes to CO and one-fourth to CO_2.

The gases leave the converter at 1500°C. Neglect heat in the incoming air.

The blast is supplied at a constant rate of 600 cu. m per minute, measured at standard conditions.

Required: 1. The total volume of air used.

2. The time of each of the two periods.

3. The weight and percentage composition of the slag.

4. The net heat generated in the converter per minute in each period, deducting the heat carried out in the gases.

Solution:

Si = 280 kg.	$Si + O_2 = SiO_2$	$O = {}^{32}\!/_{28} \times 280 =$	320 kg.
Mn = 240	$Mn + O = MnO$	$O = {}^{16}\!/_{55} \times 240 =$	70
$C \rightarrow CO$ = 600	$C + O = CO$	$O = {}^{16}\!/_{12} \times 600 =$	800
$C \rightarrow CO_2$ = 200	$C + O_2 = CO_2$	$O = {}^{32}\!/_{12} \times 200 =$	534
$Fe \rightarrow FeO$ = 300	$Fe + O = FeO$	$O = {}^{16}\!/_{56} \times 300 =$	86
		Total O required =	1,810 kg.

$1{,}810 \times \frac{22.4}{32}$ = 1,267 cu. m. of O_2 = 6,040 cu. m. of air (1).

600 cu. m. × 1.293 × 0.232 = 180 kg. of O supplied per minute.

$$\frac{320 + 70}{180} = 2.17 \text{ min. for first period without Fe.}$$

$$\frac{800 + 534}{180} = 7.41 \text{ min. for second period without Fe.}$$

${}^{86}\!/_{180}$ = 0.48 min. for Fe, to be divided between the first and second periods in proportion to the times above.

Total time of first period $= 2.17 + \frac{2.17}{9.58} \times 0.48 = 2.28$ min.

Total time of second period $= 7.41 + \frac{7.41}{9.58} \times 0.48 = 7.78$ min. (2).

SiO_2 = 280 + 320 = 600 kg. = 46.3 per cent
MnO = 240 + 70 = 310 = 23.9
FeO = 300 + 86 = 386 = 29.8
Total slag = 1,296 kg (3)

Heat generated by oxidation of:

Si = 280 × 7,160 = 2,005,000 Cal.
Mn = 240 × 1,757 = 422,000
Fe $= \frac{2.17}{9.58} \times 300 \times 1{,}151 =$ 78,000

By combination of MnO with SiO_2 (assume 70 Cal. per kilogram of MnO): 310 × 70 = 22,000 Cal.

By combination of FeO with SiO_2 (assume 120 Cal per kilogram of FeO): $120 \times \frac{2.17}{9.58} \times 386$ = 10,000 Cal.

Total for first period = 2,537,000 Cal.

Volume of gases: N_2 of air = 0.79 × 600 × 2.28 = 1,080 cu. m

Heat contained at 1500° = 1,080(0.302 + 0.000022 × 1,500)1,500 = 544,000 Cal.
2,537,000 − 544,000 = 1,993,000 Cal. ÷ 2.28 = 875,000 Cal. net heat per minute in first period (4).

$C \rightarrow CO$ = 600 × 2,430 = 1,458,000 Cal.
$C \rightarrow CO_2$ = 200 × 8,100 = 1,620,000
$Fe \rightarrow FeO$ = 232 × 1,151 = 267,000

Combination of FeO with MnO and SiO_2 (assume 120 Cal. per kilogram of FeO) = $120 \times \frac{7.41}{9.58} \times 386$ = 36,000 Cal.

Total for second period = 3,381,000 Cal.

Volume of gases:

$$\begin{aligned} N_2 &= 0.79 \times 600 \times 7.78 = 3{,}690 \text{ cu. m.} \\ CO &= 600 \times \frac{22.4}{12} = 1{,}120 \\ CO_2 &= 200 \times \frac{22.4}{12} = 373 \end{aligned}$$

$$\begin{aligned} \text{Heat in CO and } N_2 &= 4{,}810(0.302 + 0.000022 \times 1{,}500)1{,}500 = 2{,}412{,}000 \text{ Cal} \\ CO_2 &= 373(0.406 + 0.00009 \times 1{,}500)1{,}500 = \underline{303{,}000} \\ \text{Total} &= 2{,}715{,}000 \text{ Cal.} \end{aligned}$$

$3{,}381{,}000 - 2{,}715{,}000 = 666{,}000$ Cal $\div 7.78 = 85{,}600$ Cal. net heat per minute in second period (4).

It is evident that there is a large excess of heat in the first period, and the temperature will rise rapidly. The rise in temperature can be estimated by dividing the net heat generated by the heat capacity of the bath. In the second period there is barely enough heat to compensate for loss by conduction through the walls of the converter. There will be little net change in temperature during this period, though the temperature is likely to rise somewhat during the early part and fall toward the end.

In the basic Bessemer the phosphorus is oxidized to P_2O_5 in the third period. The calculations are similar to those for the acid process, with allowance for the flux.

The calculation of power required to produce the blast is discussed in Chap. VIII.

The Open-hearth Process

Like the Bessemer, the open-hearth process is fundamentally one of oxidation of impurities. But it is far more complex. No blast is used; instead, the oxidation occurs through contact with the slag, which derives its oxidizing character largely through charging of Fe_2O_3 and in part through absorbing oxygen from the excess air in the gases which pass through the furnace over the extended surface of the bath. This is a slow process; the heat of oxidation is dissipated as it is liberated, and much fuel must be burned. It is necessary to preheat the air used for combustion, and in furnaces fired with producer gas the gas also is preheated. The preheating is accomplished by passing the waste gases through checkers, which form an integral part of the furnace. The outgoing hot gases and the incoming air and gas flow alternately through the checkers, the flow being controlled by valves in the manner of the blast-furnace stove, but with the difference that here the heat is not derived by burning a combustible gas but is all supplied as sensible heat in the furnace gases. After the gases have passed through the checkers, still more heat is extracted from them by sending them through a waste-heat boiler before they are allowed to escape from the stack.

The charge usually consists of steel scrap as well as pig iron. The proportions of the two vary; about the same amount of each is often used. The scrap is charged cold; the pig iron is usually poured in molten. It is necessary also to use a flux, as well as the iron ore for oxidation. The process may be either acid or basic. The latter is the more common, as it removes phosphorus from the iron; it requires lime or dolomite to produce a strongly basic slag. The operation is so slow that it is subject to fairly close control, and it is common to leave some of the carbon in the bath at the end, and some manganese also in the basic process ("residual manganese"). Careful adjustment of slag and temperature is necessary to effect removal of the phosphorus before the carbon is eliminated.

Two types of problem are indicated with respect to the open-hearth process, one dealing with the supply and distribution of heat, including the thermal efficiency of the furnace, checkers, etc., and the other dealing with the chemistry of the process, particularly the oxidation of impurities and the slag. The first type has been taken up in Chap. III[1] but is included also in the example below and in Prob. 161. In addition, much work has been done in recent years on the mechanism of oxidation by the slag, the elimination of sulphur, the behavior of manganese, dissolved oxygen and oxides in the steel, and other important details. Equilibrium in the open-hearth process is discussed briefly in Chap. XII.

Example 14

An open-hearth furnace uses 390 gal. of fuel oil per hour, or 42 gal per ton of steel made. The composition of the fuel oil is as follows:

	Per Cent		Per Cent
C	84 35	N	0 60
H	11 33	S	0 90
O	2 82	Sp. gr	27° Bé.

As burned, using 15 per cent excess of preheated air, the calorific intensity is 2320°C. Neglect sensible heat in the oil.

Per ton of steel made there were oxidized from the charge 4.17 kg of C to CO_2, 12.50 kg of C to CO, 4.62 kg. of Si, 8.79 kg. of Mn, and 0.96 kg. of P. 47.7 kg. of Fe_2O_3 was added, half being reduced to Fe and half to FeO. 87.7 kg. of $CaCO_3$ was decomposed, and 121 kg. of slag formed. Heat of formation of the slag, 125 Cal. per kilogram.

The temperature of the furnace gases at different points was determined as follows:

Near the burners: 2000°C.
At the flue end (entrance to checkers): 1580°.
Leaving checkers (entrance to waste-heat boiler): 950°.
Leaving boiler (entrance to stack): 240°.

(A diagram of a typical open-hearth furnace is given in Fig. 1, page 33.)

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[1] See p. 34 and Probs. 59 to 62.

Required 1. Per ton of steel made, the total heat supply, and the percentage supplied by (*a*) the fuel; (*b*) the preheated air; and (*c*) the chemical reactions in the furnace.

2. The percentage of the total combustion heat (*i.e.*, total supply exclusive of chemical reactions) that is:

a. Lost in combustion.
b. Left in the furnace proper.
c. Extracted in the checkers.
d. Extracted in the boiler.
e. Lost out the stack.

Solution: The heat supplied by the fuel may be obtained directly by applying Dulong's formula for the calorific power. The result is 10,012 Cal. per kilogram of oil.

The heat contained in the preheated air cannot be obtained directly since the temperature of the air is not given. But the calorific intensity, 2320°C., is the theoretical temperature of the gases resulting from the combustion of the oil on the assumption that all the heat available is represented by the heat content of these gases. In other words the heat content of the products of combustion at 2320° is equal to the sum of the calorific power (10,012 Cal.) plus the heat in the preheated air, so that the latter can be found by difference.

The volume of the products of combustion per kilogram of oil must now be found. This is done in the usual manner, and the result is as follows: N_2, 9.506 cu. m.; O_2, 0.330; CO_2, 1.574, H_2O, 1.270; SO_2, 0.006. The heat content of these gases at 2320° is now found. Since other parts of the problem require the heat content at other temperatures, the work will be simplified by first obtaining the expression in terms of *t*, which represents the heat content at any temperature, the various given temperatures may then be substituted for *t*.

$$\begin{aligned} \text{Heat in } N_2 \text{ and } O_2 &= 9.836(0.302 + 0.000022t)t = 2.970t + 0.000216t^2 \\ CO_2 \text{ and } SO_2 &= 1.580(0.406 + 0.00009t)t = 0.641t + 0.000142t^2 \\ H_2O &= 1.270(0.373 + 0.00005t)t = 0.473t + 0.000063t^2 \\ \text{Total heat content (1)} &= 4.084t + 0.000421t^2 \end{aligned}$$

When $t = 2{,}320$, the content is 11,741 Cal.

11,741 − 10,012 = 1,729 Cal. supplied in preheated air (per kilogram of oil burned).

The quantities per kilogram of oil must be converted to the ton-of-steel basis, 42 gal. of oil being used per ton of steel.

42 gal. × 3.785 = 159 liters
Oil of 27°Bé. has a density of 0.892.
0.892 × 159 = 142 kg

142 × 10,012 = 1,422,000 Cal. from fuel per ton of steel.
142 × 1,729 = 246,000 Cal. from preheated air

Heat generated by chemical reactions:

$C \rightarrow CO_2$ = 4.17 × 8,100 = 33,770 Cal.
$C \rightarrow CO$ = 12.50 × 2,430 = 30,380
$Si \rightarrow SiO_2$ = 4.62 × 7,160 = 33,080
$Mn \rightarrow MnO$ = 8.79 × 1,757 = 15,440
$P \rightarrow P_2O_5$ = 0.96 × 5,912 = 5,680
Slag formation = 121 × 125 = 15,120
133,470 Cal.

Heat absorbed by chemical reactions:

$$\begin{array}{lllll}
Fe_2O_3 \rightarrow Fe & = 23.85 & \times 1{,}777 & = 42{,}380 & \text{Cal.} \\
Fe_2O_3 \rightarrow FeO & = 23.85 & \times \phantom{1{,}}624 & = 14{,}880 & \\
CaCO_3 \rightarrow CaO & = 87.7 & \times \phantom{1{,}}433 & = \underline{37{,}970} & \\
 & & & \ 95{,}230 & \text{Cal.}
\end{array}$$

Net heat of reactions = 133,470 − 95,230 = 38,240 Cal.

$$\begin{array}{lrl}
\text{Heat supplied by fuel} & = 1{,}422{,}000 \text{ Cal.} & = 83.4 \text{ per cent} \\
\text{By preheated air} & = \phantom{1{,}}246{,}000 & = 14.4 \\
\text{By reactions} & = \phantom{1{,}2}\underline{38{,}000} & = \underline{2\ 2} \\
\quad\text{Total heat supply} & = 1{,}706{,}000 \text{ Cal.} & = 100.0 \text{ per cent (1).}
\end{array}$$

(Note the contrast: In the open-hearth furnace about 2 per cent of the heat is supplied by chemical reactions; in the Bessemer converter all the heat is from that source.)

The heat lost in combustion is the total heat supplied in combustion minus the heat remaining near the burners at 2000°. This is found by substituting $t = 2{,}000$ in A. At the flue end of the furnace, the gases have been increased by the CO_2 liberated from $CaCO_3$. The heat content of this CO_2 at $t°$ must be added to A before substituting the other values for t.

$$CO_2 \text{ from } CaCO_3 = \frac{44}{100} \times 87.7 \times \frac{22.4}{44} = 19.6 \text{ cu. m. per ton of steel} = \frac{19.6}{142},$$

or 0.138 cu. m. per kilogram of oil.

Adding to A: Heat content $= 0.138(0.406 + 0.00009t)t = 0.056t + 0.000012t^2$. Heat content $B = 4.140t + 0.000433t^2$.

When:

$$\begin{array}{rll}
t = & 2{,}000, \text{ total heat} = 9{,}852 \text{ Cal} & (\text{using } A) \\
t = & 1{,}580, \text{ total heat} = 7{,}622 & (\text{using } B) \\
t = & 950, \text{ total heat} = 4{,}324 & \\
t = & 240, \text{ total heat} = 1{,}018 &
\end{array}$$

$$\begin{array}{rrlr}
11{,}741 - 9{,}852 = & 1{,}889 \text{ Cal.} & \text{lost in combustion} & = 16\ 1 \text{ per cent} \\
9{,}852 - 7{,}622 = & 2{,}230 & \text{left in the furnace proper} & = 19\ 0 \\
7{,}622 - 4{,}324 = & 3{,}298 & \text{extracted in the checkers} & = 28\ 1 \\
4{,}324 - 1{,}018 = & 3{,}306 & \text{extracted in the boiler} & = 28\ 1 \\
 & \underline{1{,}018} & \text{lost out the stack} & = \underline{8\ 7} \\
 & 11{,}741 \text{ Cal.} & & = 100\ 0 \text{ per cent}
\end{array}$$

In this analysis of heat supply and distribution in the open-hearth furnace, one factor has been ignored which must usually be taken into account in practice. The furnace is not fully closed or sealed. Often there are cracks and openings which admit large volumes of air. This volume of "leakage" air should be determined and added to the gases in the furnace proper. There are two ways of determining this amount, as follows:

1. *Chemical analysis of the gases beyond the points of leakage, say at the entrance to or exit from the checkers.* Let it be supposed, for example, that the analysis showed 10.0 per cent CO_2. The gases *without* leakage air were shown above to contain 1.574 cu. m. of CO_2 per kilogram of oil, this being 12.4 per cent of the total of 12.686 cu. m. of gas. Now, if 1.574 cu. m. is 10.0 per cent, the total is 15.74 cu. m., and the volume of the leakage is 15.740 − 12.686 = 3.054 cu. m. per kilogram of oil.

Instead of using the percentage of CO_2, the percentage of oxygen in the gases could be determined, and from this the volume of leakage air calculated in the same manner as in Example 3, page 23. The calculation could be made both from the CO_2 and from the oxygen, and the results checked against each other.

2. *Measurement of the volume of the gases beyond the point of leakage.* The measured volume would be reduced to standard conditions and to the basis of 1 kg. of oil. If the result were, for example, 16.0 cu. m., then the volume of leakage air would be 16.0 − 12.686 cu. m.

This measurement of volume would probably be carried out by a pitot-tube measurement of the gas velocity at some point where the area of the flue or chamber could be readily determined. Then the area × velocity = volume per unit of time. Suppose, for example, the velocity were measured as 700 m. per minute at a point where the area was 2.0 sq. m., the temperature and pressure at this point being 800°C., 750 mm. The volume of the gases then would be $700 \times 2.0 \times \frac{273}{1{,}073} \times \frac{750}{760} = 352$ cu. m. per minute, at standard conditions. The furnace uses 390 gal. of oil per hour (see statement of problem), or 1,315 kg. per hour, or 21.9 kg. per minute. The volume of the gases is therefore $\frac{352}{21.9} = 16.06$ cu. m. per kilogram of oil.

Calculation of Charge and Products in the Open-hearth Process.—Owing to the varied procedure in open-hearth practice, charge and product calculations are likely to be complicated unless the practical data can be greatly simplified. In the following example simplified data are used, but enough of the complexity has been retained to suggest the kind of problem which may be met with in a plant. The more simple open-hearth problems are worked in a similar manner to those of the Bessemer and hence require no special illustration here.

Example 15

A basic open-hearth furnace treats a charge of 40 tons of liquid pig iron and 40 tons of scrap (ton of 2,000 lb.).

Pig iron, per cent		Scrap, per cent		Ore, per cent	
C	3.6	C	0.5	Fe_2O_3	73
Si	0.9	Si	0.1	SiO_2	15
Mn	1.9	Mn	0.3	MnO	12
P	0.15	P	0.05		

2 hr. after charging the scrap, the pig is added; at this time two-thirds of the Si and Mn of the scrap and one-seventh of the Fe of the scrap have been oxidized by

the furnace gases. 1 hr. after the addition of the pig, all the remaining Si of both scrap and pig and all the remaining Mn except an amount equal to 20 per cent of the total original Mn have been oxidized as a result of the action of the FeO. From this point on, there is no further loss of Mn by the bath, owing to the fact that this loss is balanced by the reduction of some Mn from the ore. (The manganese remaining in the bath at this point is called "residual manganese.") Action of the FeO on the pig results in all the FeO being reduced back to Fe except enough to leave 20 per cent FeO in the final slag. This slag also carries 45 per cent CaO, from the addition to the charge of $CaCO_3$.

Most of the oxidation of the C and P of the charge is by the action of the Fe_2O_3 in the ore charged, supplemented by any FeO remaining from the oxidized scrap.

It is desired to have the bath just before tapping contain, in addition to the residual manganese, carbon equivalent to 0.3 per cent of the pig and scrap charged and only a negligible amount of Si and P.

Required: 1. The weight of ore to be added.

2. The weight of slag made.

3. The weight of $CaCO_3$ to be added.

4. The weight and percentage composition of the finished metal.

Solution: The oxidation of the impurities is accomplished in part by oxygen from the furnace gases (*i.e.*, excess air) and in part by oxygen derived by reduction of Fe_2O_3 in the added ore. The weight of ore is determined by the amount of oxygen required from the ore, which would be the oxygen required by the impurities minus the amount that is derived from the furnace gases. This may be calculated first, as follows:

C to be oxidized (deducting that left in the bath at the end) $= 0.036 \times 80{,}000 + 0.005 \times 80{,}000 - 0.003 \times 160{,}000 = 2{,}800$ lb. Assume that the carbon goes to CO, since further oxidation to CO_2 would be by O in the gases and would not affect the ore requirement

Si to be oxidized $= 0.009 \times 80{,}000 + 0.001 \times 80{,}000 = 800$ lb

Mn to be oxidized $= (0.019 \times 80{,}000 + 0.003 \times 80{,}000) \times 0.80 = 1{,}408$ lb. (20 per cent of the Mn is residual.)

P to be oxidized $= 0.0015 \times 80{,}000 + 0.0005 \times 80{,}000 = 160$ lb.

The oxygen required for these, deducting in the case of Si and Mn the two-thirds in the scrap which is oxidized by the gases during melting, is as follows:

$$\begin{aligned}
&\text{For C: } \tfrac{16}{12} \times 2{,}800 &&= 3{,}733 \text{ lb.}\\
&\text{For Si: } \tfrac{32}{28}(800 - \tfrac{2}{3} \times 80) &&= 854\\
&\text{For Mn: } \tfrac{16}{55}(1{,}408 - \tfrac{2}{3} \times 240) &&= 363\\
&\text{For P: } \tfrac{80}{62} \times 160 &&= \underline{206}\\
& &&\ 5{,}156 \text{ lb.}
\end{aligned}$$

Not all of this, however, is to be supplied by ore. During melting, one-seventh of the Fe in the scrap forms FeO, and part of this is subsequently reduced to Fe, thus supplying oxygen. Fe in the scrap $= 0.9905 \times 80{,}000 = 79{,}240$ lb. O taken up $= \frac{79{,}240}{7} \times \frac{16}{56} = 3{,}234$ lb. From this must be deducted the oxygen in the FeO not reduced, which is the FeO equal to 20 per cent of the slag. Determination of this FeO requires determining the amount of the slag, which in turn depends on the weight of ore used. Hence the determination must be an indirect one, and an algebraic method suggests itself. If x be the weight of ore added, the amount of slag and of FeO in the slag can be found in terms of x. The oxygen to be supplied by the ore is thus obtained in terms of x, and x is determined by an equation derived from the ore composition:

The slag will contain SiO_2, MnO, and P_2O_5, formed by oxidation of impurities, and SiO_2 and MnO from the ore, the sum of these being 35 per cent of the slag; 45 per cent is CaO, and 20 per cent FeO.

SiO_2 formed from Si $= \frac{60}{28} \times 800 = 1{,}714$ lb.
MnO from Mn $= \frac{71}{55} \times 1{,}408 = 1{,}818$
P_2O_5 from P $= \frac{142}{62} \times 160 = 366$
SiO_2 and MnO from ore $= 0.15x$ and $0.12x$.

Adding:

$3{,}898 + 0.27x = 35$ per cent of slag.

FeO = 20 per cent of slag $= 0.20 \times \frac{3{,}898 + 0.27x}{0.35}$, or $2{,}228 + 0.1543x$

O in this $= \frac{16}{72}(2{,}228 + 0.1543x)$, or $496 + 0.0343x$

O available for impurities from FeO $= 3{,}234 - (496 + 0.0343x)$.

O to be supplied by ore $= 5{,}156 - (2{,}738 - 0.0343x) = 2{,}418 + 0.0343x$.

From ore analysis:

O available in the ore $= \frac{48}{160} \times 0.73x$.

Equating:

$$2{,}418 + 0.034x = 0.3 \times 0.73x$$
$$x = 13{,}080 \text{ lb } (1).$$

Weight of slag $= \frac{3{,}898 + 0.27x}{0.35} = 21{,}200$ lb (2).

CaO $= 0.45 \times 21{,}200 = 9{,}540$ lb.
$CaCO_3 = \frac{100}{56} \times 9{,}540 = 17{,}020$ lb (3)

Fe added to the bath from the ore = Fe in the ore minus Fe in the slag.
Fe in ore $= \frac{112}{160} \times 0.73 \times 13{,}080 = 6{,}700$ lb.
Fe in slag $= \frac{56}{72} \times 0.20 \times 21{,}200 = 3{,}300$
Fe from ore $= 3{,}400$ lb.

Total Fe $= 0.9345 \times 80{,}000 + 0.9905 \times 80{,}000 + 3{,}400$
$= 157{,}400$ lb $= 99.48$ per cent
C $= 0.003 \times 160{,}000 = 480 = 0.30$
Mn $= \frac{0.20}{0.80} \times 1{,}408 = 350 = 0.22$
Total metal $= 158{,}230$ lb. $= 100.00$ per cent (4).

In the open-hearth problem above, the weight of ore to be added has been calculated on the basis of certain given data regarding oxidation by the gases which would not ordinarily be known. In the plant the addition of ore would be governed by experience and by analysis of samples rather than by calculation. If the amount of ore and flux actually used in a given heat were determined by weighing it as used, calculations could then be made in a manner somewhat the reverse of the above, and certain interesting and perhaps very useful information deduced concerning the action in the furnace, such as the proportion of the total oxidation performed by the gases and by the ore and the amount of residual manganese. In the works the engineer or furnaceman possesses or can readily obtain an array of data of a certain character—weights, analyses, gage readings, measurements of various kinds. By means of these he may then calculate other data not directly obtainable, study his operation "on paper," and predict without the cost and labor of actually trying it the effect of possible changes in the charge or conditions of operation. These remarks are of course applicable, not especially to open-hearth practice, but to chemical and metallurgical processes in general.

Electric Steel

Steelmaking in the electric furnace is usually a process of superrefining (deoxidizing), sometimes preceded by refining (oxidizing). The same quantitative principles apply as for other steel furnaces, and the absence of fuel and the resulting products of combustion is a simplifying factor. The process may be one in which there is no oxidation of impurities. Some air may be admitted, or air may be excluded. Fluxes are utilized to a greater extent. In superrefining, the first slag is poured off and a second slag is formed, containing calcium carbide (CaC_2). The carbide slag is effective in the removal of sulphur and in the thorough deoxidization of the bath.

A problem will be given employing actual data from an electric-furnace heat.[1] From these will be calculated a number of facts none of which is given in the reference from which the data came and some of which would not be directly obtainable by the furnace operator. Not all the data given are used in the solution, and some are slightly conflicting. Some of the facts calculated will be based on assumptions not wholly true, and the results will be proportionately approximate. The example will serve to illustrate the manner in which such practical data may be used and to bring out the fact that only approximate results can be expected from analyses which are not entirely reliable with respect to all items.

Example 16

An electric furnace log shows the following data:

Scrap charged (16,600 lb.), per cent		Limestone charged (750 lb.), per cent		Melted metal, per cent		First (oxidizing) slag, per cent	
C	0.25	$CaCO_3$	94	C	0.15	SiO_2	13.47
Mn	0.45	$MgCO_3$	3	Mn	0.26	FeO	8.31
Si	0.10	SiO_2	1	Si	0.015	Al_2O_3	2.26
S	0.034	Fe_2O_3	1	S	0.03	MnO	5.08
P	0.035	Al_2O_3	1	P	0.014	CaO	50.35
Ni	2.00			Ni	2.07	MgO	10.61
Cr	0.60			Cr	0.28	CaS	0.093
						Cr_2O_3	8.37
						P_2O_5	1.36

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[1] From Sisco, Frank T., "The Manufacture of Electric Steel," p. 182, McGraw-Hill Book Company, Inc., New York, 1924.

Current is turned on the furnace at 2:00, and the charge is completely melted at 4:45. The first slag is finished and removed at 5:05 and the second slag started. The additions during slagging and the final products are as follows:

Lime, 600 lb. (77 CaO; 8 MgO; 1 Al_2O_3; 1 Fe_2O_3; 5 SiO_2).
Coke, 225 lb. (80 C; 20 SiO_2).
Fluorspar, 160 lb. (90 CaF_2; 3 SiO_2; 5 $CaCO_3$; 1 Fe_2O_3; 1 Al_2O_3).
Nickel, 260 lb.
Ferromanganese, 60 lb. (80 Mn; 11.8 Fe; 7 C; 1 Si; 0.2 P).
Ferrochromium, 285 lb (68 Cr, 26 Fe; 6 C).
Sand, 200 lb. (100 SiO_2).
Ferrosilicon, 90 lb (50 Fe; 50 Si).
Washed metal, 600 lb. (96 Fe; 4 C).

	Finished Steel, Per Cent
C	0.48
Mn	0.49
Si	0.228
S	0.010
P	0.021
Ni	3.44
Cr	1.41
Fe	93.92

	Second Slag, Per Cent
SiO_2	21.31
FeO	0.09
Al_2O_3	2.01
MnO	0.06
CaO	53.78
MgO	15.01
CaS	2.19
CaC_2	0.57

The CaF_2 gives the reaction $2CaF_2 + SiO_2 = SiF_4 + 2CaO$.

Required: 1. The weight of the melted metal

2. The weight of the first slag.
3. The weight of the finished steel.
4. The weight of the second slag
5. The weight of CaO and MgO taken from the lining by each slag.
6. The percentage of desulphurization and of dephosphorization by each slag.
7. The percentage of the carbon added to the bath that is required for recarburization.

Solution: The weight and analysis of the metal charged being given, and the analysis of the melted metal, the weight of the latter can be obtained from any element which is not slagged or otherwise removed during melting. This would be approximately true of the nickel; it would not be true of any of the other elements. Assuming then, that the same *weight* of Ni constitutes 2.00 per cent of the scrap charged and 2.07 per cent of the melted metal, the weight of the latter is $\frac{2.00}{2.07} \times 16{,}600 = 16{,}030$ lb. (1). The accuracy of this result depends, of course, on the accuracy of the analyses for nickel as well as on the truth of the assumption made.

The approximate weight of the first slag can be obtained in a similar manner. Select some element charged, deduct the amount in the metal to obtain the amount in the slag, and calculate from the percentage which this forms in the slag. Here it must be noted that the *flux* is a large factor in the slag and that the data of the problem show the analysis of the limestone only in round numbers. [This is due to the fact that the composition of the limestone used was not given in the reference; a typical composition of limestone of average quality used for electric-furnace work has been assumed. The same is true of the lime (see below); of the other materials added, the actual composition either was given or else was so nearly standard that any possible variation in it can be of little effect.] Consequently the calculation must be based on some element coming mostly from the scrap. A further reason for not basing the calculation on the CaO or MgO is that these compounds are always taken up in considerable quantities from the furnace lining. The same is often true of SiO_2. FeO may also be taken up; also, no Fe percentages are given, and it is always of doubtful accuracy to find them by difference on the assumption that the balance of the metal is Fe. Evidently MnO, Cr_2O_3, and P_2O_5 afford possible bases of calculation, though the P_2O_5 is small in amount.

Mn to slag $= 0.0045 \times 16{,}600 - 0.0026 \times 16{,}030 = 33.0$ lb.

MnO $= \frac{71}{55} \times 33.0 = 42.6$ lb. $\frac{42.6}{0.0508} = 839$ lb. of slag.

Cr to slag $= 0.60 \times 16{,}600 - 0.28 \times 16{,}030 = 54.7$ lb.

$Cr_2O_3 = \frac{152}{104} \times 54.7 = 80.0$ lb. $\frac{80.0}{0.0837} = 956$ lb. of slag.

P to slag $= 0.00035 \times 16{,}600 - 0.00014 \times 16{,}030 = 3.57$ lb

$P_2O_5 = \frac{142}{62} \times 3.57 = 8.18$ lb. $\frac{8.18}{0.0136} = 601$ lb. of slag.

Of the three results, it would perhaps be best to take a rough average of the first two and conclude that the weight of the slag was about 900 lb. (2).

The weight of the finished steel might be approached from the standpoint of the weight of the melted charge plus materials added minus materials slagged But this would evidently be inaccurate as well as laborious. Calculation on the nickel basis is again possible.

Total Ni charged $= 332 + 260 = 592$ lb.

Weight of finished steel $= \frac{592}{0.0344} = 17{,}200$ lb. (3).

For calculating the second slag, MnO is less satisfactory, since so little is slagged at this stage. The SiO_2, and possibly CaO, may be used to better advantage.

$$\begin{array}{llr}
\text{Si in melted charge} & = 0.00015 \times 16{,}030 = & 2.4 \text{ lb.} \\
\text{Si in ferromanganese} & = 0.01 \times 60 \qquad = & 0.6 \\
\text{Si in ferrosilicon} & = 0.50 \times 90 \qquad = & 45.0 \\
 & \text{Total} = & \overline{48.0} \text{ lb} \\
\text{Si in finished steel} & = 0.00228 \times 17{,}200 = & 39.3 \text{ lb} \\
 & \text{Si oxidized} = & \overline{8.7} \text{ lb}
\end{array}$$

$$\begin{array}{lll}
SiO_2 \text{ formed} & = \frac{60}{28} \times 8.7 & = 19 \text{ lb} \\
SiO_2 \text{ in lime} & = 0.05 \times 600 & = 30 \\
SiO_2 \text{ in coke} & = 0.20 \times 225 & = 45 \\
SiO_2 \text{ in fluorspar} & = 0.03 \times 160 & = 5 \\
SiO_2 \text{ in sand} & & = \underline{200} \\
 & \text{Total } SiO_2 & = 299 \text{ lb.}
\end{array}$$

SiO_2 decomposed by $CaF_2 = \frac{60}{2 \times 78} \times (0.90 \times 160) = 55$ lb.

Weight of second slag $= \frac{299 - 55}{0.2131} = 1{,}144$ lb.

$$\begin{array}{lll}
\text{CaO in lime} & = 0.77 \times 600 & = 462 \text{ lb.} \\
\text{CaO in fluorspar} & = \frac{56}{100} \times 0.05 \times 160 & = 4 \\
\text{CaO formed from } CaF_2 & = \frac{56}{78} \times 144 & = \underline{103} \\
 & \text{Total CaO} & = 569 \text{ lb.}
\end{array}$$

Weight of second slag $= \frac{569}{0.5378} = 1{,}060$ lb.

The approximate weight of the second slag is therefore about 1,100 lb. (4).

The calculations of the CaO and MgO absorbed from the lining must necessarily be rough approximations in view of the assumed compositions of the lime and limestone.

CaO in limestone = $\frac{56}{100} \times 0.94 \times 750$ = 394 lb.
CaO in slag = 0.5035×900 = 453
CaO from lining = 59 lb. (first slag)

(The CaO used to form CaS is negligible.)

CaO added for second slag (previously calculated) = 569 lb.
CaO in second slag = $0.5378 \times 1{,}100$ = 591
CaO from lining = 22 lb. (second slag)

(This result really has no meaning since the weight of the slag was calculated as 1,060 lb. on the assumption that *no* CaO was absorbed from the lining; however, the method of calculation is illustrated for use when more complete data are available.)

MgO in limestone = $\frac{40}{84} \times 0.03 \times 750$ = 10.7 lb
MgO in slag = 0.1061×900 = 95.5
MgO from lining = 84.8 lb. (first slag)

MgO in lime = 0.08×600 = 48 lb
MgO in slag = $0.1501 \times 1{,}100$ = 165
MgO from lining = 117 lb. (second slag)

S in first slag = $\frac{32}{72} \times 0.00093 \times 900$ = 0.4 lb.
S in charge = $0.00034 \times 16{,}600$ = 5.6 lb.

$\frac{0.4}{5.6}$ = 7 per cent desulphurization by first slag.

S in second slag = $\frac{32}{72} \times 0.0219 \times 1{,}100$ = 10.7 lb. This is more than in the scrap charged, indicating the addition of S in the coke and ferroalloys.

S in the finished steel = $0.0001 \times 17{,}200$ = 1.7 lb. $5.2 - 1.7 = 3.5$ lb. Therefore, the second slag removed the S added in the coke and ferroalloys, and, in addition, $\frac{3.5}{5.6}$, or 63 per cent of the sulphur in the original scrap.

P in scrap = $0.00035 \times 16{,}200$ = 5.7 lb.
P in first slag = $\frac{62}{142} \times 0.0136 \times 900$ = 5.3 lb.

However, some of the 5.3 lb. of P in the slag probably came from the limestone. Since most of the P oxidized would be oxidized during the melting of the scrap, a better idea of the dephosphorization is gained from the percentage of P in the melted metal: $0.00014 \times 16{,}030 = 2.2$ lb.

Per cent dephosphorization = $\frac{5.7 - 2.2}{5.7}$ = 61 per cent (first slag).

P added in ferromanganese = $0.002 \times 60 = 0.12$.

P in finished steel = $0.00021 \times 17{,}200 = 3.6$ lb. Evidently P has been added in the other ferroalloys, and there has been little or no dephosphorization in the second slag.

C in melted metal = $0.0015 \times 16{,}030$ = 24 lb.
C in finished steel = $0.0048 \times 17{,}200$ = 83
C taken up by bath = 59 lb.

C added:

In coke = 0.80 × 225 = 180 lb.
In ferromanganese = 0.07 × 60 = 4
In ferrochromium = 0.06 × 295 = 17
In washed metal = 0.04 × 600 = 24
225 lb.

$^{59}/_{225}$ = 26 per cent used in recarburization (7).

Electric-furnace Efficiency and Requirement of Power.—As efficiency and power requirement are of such importance in electric-furnace processes, a simple illustration for the case of electric steel may be given at this point. The calculation of efficiency is based on the amount of heat utilized by the charge in the furnace divided by the electrical energy input to the furnace. In dividing, the heat and electrical energy must, of course, be converted to the same units. A convenient conversion factor in working in terms of Calories is 860 Cal. = 1 kw.-hr.

The energy input to the furnace is thus divided into two parts, the heat utilized and the heat lost. When the temperature of the furnace charge is being maintained constant and no endothermic reactions are taking place in the furnace, it is obvious that the input is equal to the losses; the efficiency at this stage would be zero. When the charge is being heated, the efficiency is relatively high. In cases of the kind under consideration here, it is more proper to speak of the thermal "efficiency of the operation" than the "efficiency of the furnace," since the efficiency varies with the way in which the furnace is operated.

Example 17

An electric furnace is used for melting steel. Using 500 kw., 3,000 kg. of cold steel scrap is heated to 1450°C. and melted in 3 hr. and then superheated to 1550° in ½ hr. more

1 kg. of steel just melted is found to contain 280 Cal., and 1 kg. of superheated steel 300 Cal.

Required: 1. The electrothermal efficiency of the melting part of the operation

2. The electrothermal efficiency of the superheating operation.

3. The electrothermal efficiency of the whole operation.

4. The minimum power required to keep the furnace charge constantly at 1550°.

Solution:

Heat utilized in melting stage = 3,000 × 280 = 840,000 Cal.
Heat input in melting stage = 500 × 3 × 860 = 1,290,000

$$\text{Efficiency} = \frac{840}{1{,}290} = 65 \text{ per cent (1).}$$

Heat utilized in superheating = 3,000 × 20 = 60,000 Cal.
Heat input in superheating = 500 × ½ × 860 = 215,000

$$\text{Efficiency} = {}^{60}/_{215} = 28 \text{ per cent (2).}$$

$$\text{Efficiency of whole operation} = \frac{3{,}000 \times 300}{500 \times 3.5 \times 860} = \frac{900}{1{,}505} = 60 \text{ per cent (3).}$$

Losses during superheating = 215,000 − 60,000 = 155,000 Cal. in 1 hr. $\frac{155{,}000}{860} = 180$

kw. required to hold temperature at 1550°, assuming the losses at 1550° the same as during the heating from 1450 to 1550°. This result is also obtained by $\frac{155,000}{430,000} \times 500$ kw. = 180 kw.

Another assumption sometimes made is that the losses are proportional to the mean temperatures. During the superheating period the mean temperature was 1500°, so that the losses on this assumption would be $\frac{1,550}{1,500} \times 155,000 = 160,000$ Cal., making the result 186 kw.

Problems

Note: Additional problems on the metallurgy of steel will be found in Chaps. VIII, IX, and XI.

148. An acid-lined Bessemer converter blows 15 tons of pig iron in 12 min. The following impurities are oxidized out:

	Per Cent
C	4.0
Si	1.8
Mn	0.8

Also, 3 per cent of the iron is oxidized. Assume that the iron is oxidized at a uniform rate and that three-fourths of the C goes to CO, one-fourth to CO_2.

Required: 1. The volume of air required.

2. The length of the two periods of the blow.

3. The weight of slag made.

149. An acid Bessemer converter blows 25 metric tons of pig iron having the following composition:

	Per Cent
C	4.0
Mn	1.2
Si	1.4
Fe	93.4

Besides the impurities there is oxidized iron equivalent to 2.5 per cent of the pig, the iron oxidizing at a uniform rate. Five-eighths of the carbon goes to CO and three-eighths to CO_2.

The blast is supplied at the rate of 700 cu. m. per minute, measured at standard conditions.

Required: 1. The total volume of air used.

2. The time of each of the two periods.

3. The weight of the slag.

150. A Bessemer converter is charged with 18 metric tons of pig iron from which the following impurities are oxidized:

	Per Cent
C	4.2
Si	1.5
Mn	0.7

Enough iron is also oxidized to make 24 per cent FeO in the slag. Assume that the iron is oxidized at a uniform rate. The ratio of CO to CO_2 is 3:1.

The blowing engines supply per minute 510 cu. m. of moist air (measured at standard conditions), the air carrying 19 mm. of water vapor.

Required: 1. The time of each of the two periods of the blow.

2. The weight of the slag.

3. The percentage composition of the gases in each period.

151. An acid-lined Bessemer converter blows 20 short tons of pig iron carrying 3.72 per cent C, 2.18 Si, 1.24 Mn. In addition, there is oxidized Fe amounting to 4.8 per cent of the pig iron. Assume that the Fe is oxidized at a uniform rate throughout the blow.

The blast enters at a pressure of 2.5 atm. gage, a temperature of 45°C., and one-third saturated with moisture. No free O_2 escapes from the converter. Two-thirds of the carbon goes to CO and one-third to CO_2. The blow requires 10.5 min.

Required: 1. The total weight of the slag.

2. The volume of the blast at the given conditions

3. The time of each period of the blow.

4. The percentage composition of the gases in each period.

152. An acid-lined Bessemer converter blows a charge of 20 metric tons of pig iron containing:

	Per Cent
C	3.6
Mn	0.7
Si	1 2

Fe amounting to 2.8 per cent of the pig iron is also oxidized. Two-thirds of the carbon goes to CO, one-third to CO_2. Assume the iron oxidized at a uniform rate throughout the blow. The blow lasts 13 min. The gases escape at 1500°C.

Heat of slag formation, 150 Cal per kilogram of SiO_2.

Required: 1. The total volume of air necessary for the blow.

2. The time of each of the two periods.

3 The weight of slag and the volume of gas made.

4. The heat generated per minute in each period.

5. The net heat left per minute in each period after deducting the heat carried out in the gases.

153. A Bessemer converter treats 30 tons of pig iron, receiving 680 cu. m. of air per minute. The impurities removed from the pig iron are C, 4 per cent; Si, 1 8; Mn, 1.6. Three-fourths of the carbon goes to CO, one-fourth to CO_2. Toward the end of the blow 900 kg. of Fe is oxidized.

Specific heat of molten bath, 0.20.

The gases leave the converter at 1500°C. Neglect heat in the blast entering

Required: 1. The total blowing time.

2. The average rate of heating or cooling of the bath (degrees centigrade per minute) *in each period,* assuming that the radiation, conduction, and convection loss is a constant amount equal to 25 per cent of the total heat generated per minute during the first period.

154. A charge of 10,000 kg. of pig iron is blown in a Bessemer converter, giving 527 kg. of slag of the following composition: SiO_2, 65.5 per cent; MnO, 13.5; FeO, 21.0. The gases from the converter amount to 2,760 cu. m. and carry CO_2, 6.0 per cent; CO, 18.1; N_2, 75.9.

Required: 1. The composition of the pig iron used.

2. The yield of pure iron left after the blow.

3. The cubic meters of air required for the entire blow.

4. The relative time occupied by the two periods.

155. A Bessemer converter blows a charge of pig iron to steel in 11 min. 1 per cent of the Fe in the pig iron is oxidized and slagged. The slag amounts to 4,200 lb. and analyzes SiO_2, 70 per cent; MnO, 20; FeO, 10. In addition to the Si and Mn, the pig iron carries 4.2 per cent C. Three-fourths of the carbon is oxidized to CO, one-fourth to CO_2.

Assume that the Fe is oxidized at a uniform rate.

Required: 1. The weight of the pig iron charged.

2. The volume of air supplied per minute, in cubic feet.

3. The time of each period.

156. An article quotes the following analyses for operation of a converter blowing low-silicon high-manganese pig iron by the Swedish Bessemer process, the blow being stopped so as to retain carbon and manganese in the steel:

Pig iron, per cent		Steel at end of blow, per cent		Slag, per cent	
C	4 36	C	0.74	SiO_2	47.25
Mn	2 98	Mn	0.25	MnO	37.80
Si	0.95	Si	0.04	FeO	9.45
P	0.02			Al_2O_3	4.22
Fe	91 69			MgO	0 40
				CaO	0 88
				P_2O_5	None

The charge is 20 metric tons, and the weight of the steel 18,400 kg. No flux is added, but there is corrosion from the converter lining The lining contains no manganese.

Required: 1. The percentage removal of each of the impurities.

2 What would have been the weight and percentage composition of the slag if there had been no corrosion of lining?

3. The percentage composition of the lining

157. An experimental Bessemer converter blows pig iron carrying Fe, 93 per cent; C, 4, Si, 2, Mn, 1. The charge is 22 tons. One-fourth of the carbon burns to CO_2, three-fourths to CO. Fe amounting to 5 per cent of the charge is oxidized at a uniform rate.

In case *a* the converter is blown with ordinary air; in case *b*, with air enriched to 30 per cent O_2.

Average temperature of the bath, 1500°C.

Required: 1. If in case *a* the blow lasts 15 min., how long will it last in case *b*, the blowing engines making the same number of revolutions per minute?

2. Calculate for both cases the excess of heat generated over the heat carried out by the gases, in each period.

158. A Bessemer converter, lined with basic material, is charged with 20 tons of pig iron of the following composition:

	Per Cent
Fe	91.2
C	3.6
Si	1.7
Mn	1.1
P	2 4

The blow oxidizes all the C, Si, Mn, and P and also Fe amounting to 5.6 per cent of the pig iron. Assume that the Fe is oxidized at a uniform rate throughout the blow. Enough CaO is added to make 35 per cent CaO in the slag. Two-thirds of the carbon goes to CO, one-third to CO_2. The blowing engines furnish 580 cu. m. of air per minute.

Required: 1. The volume of air necessary to blow the charge.

2. The length of each period of the blow.

3. The weight of CaO to be added, and the percentage composition of the slag.

159. A Bessemer converter was charged with 10,000 kg. of pig iron and supplied with 203 cu. m. of blast per minute for 18 min., making 1,200 kg. of slag analyzing SiO_2, 15 per cent; MnO, 5.9; P_2O_5, 47.3; FeO, 24.0; CaO, 7.8. One-quarter of the carbon burned to CO_2, and three-quarters to CO. After the blow, 50 kg. of ferromanganese was added as a deoxidizer and recarburizer (Fe, 15 per cent; Mn, 80; C, 5). Assume one-half the manganese of the ferromanganese lost by oxidation.

Required: 1. The percentage composition of the iron used.

2. The volume and the average percentage composition of the gases from the entire blow.

3. The time of each period of the blow.

4. The percentage yield of steel at the end of the blow.

160. A basic Bessemer converter is charged with 20 metric tons of pig iron, together with a flux of CaO, and is blown until it has 17.0 tons of Fe and 5,720 kg. of slag analyzing 13 per cent SiO_2, 5 MnO, 19 P_2O_5, 27 FeO, 36 CaO.

Assume that the iron is oxidized at a uniform rate throughout the blow The carbon goes two-thirds to CO and one-third to CO_2.

The total blowing time is 28 min. Assume that the heat of formation of the slag is 150 Cal. per kilogram of SiO_2 in the first period and 700 Cal. per kilogram of CaO in the third period.

Required: 1. The total volume of air required for the blow

2. The time of each period.

3. The heat generated per minute during each period.

161. A producer gas analyzes:

	Per Cent
CO_2	3
CO	26
CH_4	3
H_2	14
N_2	54

It is burned in an open-hearth furnace, using 10 per cent excess air for combustion In addition to the 10 per cent excess air used in combustion, 50 per cent excess air leaks into the furnace through the doors. The flue gases pass out through regenerators for preheating the incoming gas and air and then through a waste-heat boiler to the stack. In addition to the carbon in the gas, 0.054 kg. of carbon per cubic meter of gas is burned to CO by oxygen from the charge and from CO to CO_2 by oxygen from the air leaking in through the doors.

The following temperatures are observed:

Air to regenerators, 35°C. Preheated air, 1000°.

Gas to regenerators, 600°C. Preheated gas, 1100°.

Maximum temperature of flame, 2100°. Flue gases leaving furnace, 1550°.

Flue gases leaving regenerators, 680°. Flue gases leaving boiler, 350°.

Required: 1. The air used, per cubic meter of gas: (*a*) for combustion; (*b*) by leakage.

2. The composition of the flue gases before and after admixture with the leakage air.

3. The total heat entering the furnace.
4. The heat in the furnace gases at the maximum flame temperature.
5. The heat in the flue gases leaving the furnace.
6. The heat in the flue gases leaving the regenerators.
7. The heat in the flue gases leaving the boiler
8. The percentage heat distribution of the operation.
9. The operating efficiency of the regenerators (gas and air combined).
10 The percentages of the flue gas that go to the gas and air regenerators.
11. The percentage of the preheating in the gas that is furnished by the regenerators and by the producer.

162. A basic open-hearth steel furnace is charged with 20 tons of steel scrap and 20 tons of pig iron. During the heat there are added 3 tons of iron ore and enough $CaCO_3$ to make a final slag of 40 per cent CaO. For deoxidizing there are used 400 kg. of ferromanganese and 180 kg of ferrosilicon.

There is produced 39,800 kg. of finished steel analyzing C, 0.3 per cent, Mn, 0.2, Si, 0.1; P, 0.06; Fe, 99.34

The materials used analyze as follows:

	Steel scrap, per cent	Pig iron, per cent	Ferromanganese, per cent	Ferrosilicon, per cent	Iron ore, per cent
Fe	99.0	92.6	12	50	Fe_2O_3 80
C	0.5	1.0	6		
Mn	0.3	1.5	80		MnO 1
Si	0.12	0.8	2	50	SiO_2 16
P	0.08	1.1			

The carbon oxidized goes to CO.

Assume that one-half the iron in the slag (as FeO) comes from the ore and one-half from oxidation by the furnace gases

Required: 1 The weight and percentage composition of the slag.

2. The weight of $CaCO_3$ needed.

3. The proportion of the oxidation in the furnace that is performed by the iron ore and by the furnace gases.

163. A basic open-hearth furnace treats a charge composed of the following:

Liquid pig (45 tons), per cent	Scrap (30 tons), per cent	Ore (8 tons), per cent	Flux (8 tons), per cent
C 4.3	C 0.1	Fe_2O_3 80.0	$CaCO_3$ 99
Si 1.0	Si 0.05	SiO_2 5.0	SiO_2 1
Mn 1.7	Mn 0.5	Mn 0.1	
P 0.11	P 0.03	P 0.07	

There is made 75 tons of steel carrying C, 0.1 per cent; Mn, 0.2; P, 0.02; and 0.1 FeO in solution. The slag made carries 15 per cent SiO_2, 17 FeO, 52 CaO, 5.5 MgO, 9.5 MnO, 1 P_2O_5. The furnace is lined with burned dolomite After pouring into the ladle there is added to the steel 1,000 lb of ferromanganese (80 per cent Mn, 15 Fe, 5 C).

Required: 1. The weight of slag made.

2. The weights of CaO and MgO going to the slag from the furnace lining.

3. The weights of Fe, Mn, and P unaccounted for (probably partly due to volatilization and partly to round numbers in statement of weights and analyses)

4. The composition of the finished steel.

164. A basic open-hearth steel furnace treats a charge of 80 tons of pig iron and scrap having an average composition as follows:

	Per Cent
C	2.7
Mn	0.7
Si	1.0
P	0.8
Fe	94.8

The finished metal (ready for recarburizing) is to contain one-fifth of the original carbon and one-seventh of the original manganese, but no silicon or phosphorus.

The oxidation of the impurities is accomplished partly by the furnace gases and partly by the addition of ore containing 85 per cent Fe_2O_3 and 15 per cent SiO_2, assume the division as follows:

Si, all by gases	to SiO_2
Mn, one-half by gases, one-half by ore	to MnO
C, one-fifth by gases, four-fifths by ore	to CO
P, all by ore	to P_2O_5

The slag will contain FeO equivalent to 2 per cent of the iron in the pig and scrap charged. The FeO is formed one-half by gases, one-half from reduced Fe_2O_3. Enough $CaCO_3$ is charged to make a slag of 40 per cent CaO

Required: 1. The weight of ore necessary.

2. The weight of slag made.

3. The weight of $CaCO_3$ used.

4. The weight of the finished bath.

165. A basic open-hearth steel furnace receives 40 tons of pig iron and scrap of an average composition as follows:

	Per Cent
Fe	93.7
C	3.0
Mn	0.8
Si	1.1
P	1.4

There are added also enough ore to accomplish three-fourths of the oxidation of the impurities (C to CO, Mn to MnO, Si to SiO_2, P to P_2O_5) and enough lime to give a slag containing 40 per cent CaO. The ore is 82 per cent Fe_2O_3, 14 SiO_2, 4 Al_2O_3. The lime is pure CaO 2 per cent of the total Fe charged (including that in the ore) is lost in the slag as FeO.

The furnace uses 50,000 cu. m. of producer gas analyzing:

	Per Cent
CO	25
H_2	12
CO_2	8
H_2O	4
N_2	51

This is burned with 20 per cent excess air. The products of combustion complete the oxidation of the impurities, oxidize the Fe that enters the slag, and change the CO to CO_2. The furnace gases enter the regenerators at 1500°C., and these preheat both the fuel gas and the air to 700°C.

Required: 1. The weight of ore used, in kilograms.

2. The weight of slag.

3. The weight of the Fe yielded.

4. The volume of the gases leaving the furnace.

5. The efficiency of the regenerators

166. An open-hearth furnace is charged first with 40 tons of scrap containing 0.5 per cent C, 0.1 Si, 0.3 Mn, 0.05 P Two hours later there is added 50 tons of molten pig iron containing 4.0 per cent C, 1.0 Si, 1.5 Mn, 0.26 P. Just before the pig iron is added, there has been oxidized by the furnace gases two-thirds of the Si and Mn in the scrap; also, one-eighth of the Fe in the scrap has been changed to FeO. Along with the pig iron are added ore containing 75 per cent Fe_2O_3, 13 SiO_2, 12 MnO, and enough $CaCO_3$ to make a slag of 42 per cent CaO. The FeO formed from the scrap now reacts with the impurities in the pig iron, supplying oxygen to oxidize them in part, and is itself reduced back to Fe. Enough FeO is formed from the ore to make 20 per cent FeO in the final slag, the rest of the Fe_2O_3 in the ore being reduced to Fe.

The bath just before tapping will contain 25 per cent of the Mn contained in the pig and scrap as residual manganese. It will also contain carbon equivalent to 0.5 per cent of the total weight of the pig and scrap charged. Enough ore is used to account for the oxidation of all the balance of the impurities (assume carbon going to CO), after allowing for the action of the FeO noted above.

Required: 1. The weight of ore added

2. The weight of $CaCO_3$ used.

3. The percentage composition of the slag.

4. The percentage composition of the steel (before recarburizing).

167. A basic open-hearth furnace uses the following materials:

Pig iron, per cent	Steel scrap, per cent	Ore, per cent	Flux, per cent
C 3.9	C 0.3	Fe_2O_3 76	$CaCO_3$ 97
Si 1.0	Si 0.2	SiO_2 15	SiO_2 3
Mn 1.6	Mn 0.6	MnO 4	
P 0.8	P 0.04	Al_2O_3 5	

The operation is carried on as follows: 60 short tons of cold scrap is charged and heated for 2 hr., during which time two-thirds of its Si and Mn and one-sixth of its Fe are oxidized. 100 tons of molten pig iron is then poured in, and part of its impurities is oxidized by the FeO already formed. Ore and flux are then added to continue the oxidation and slagging of impurities.

All the FeO formed in the first stage and one-half the FeO from the ore are reduced to Fe. MnO of the ore is not reduced. One-half of the carbon and one-seventh of the manganese in the pig and scrap remain in the finished steel, but the Si and P are entirely removed.

Enough flux is used to make 45 per cent CaO in the slag. The carbon oxidized goes to CO. 2,100 lb. of burnt dolomite (assume CaO.MgO) is slagged from the hearth.

Required: 1. The weight of ore to be used, in pounds.

2. The weight of flux to be used, in pounds

3. A charge balance of the furnace.

4. The percentage of the oxidation of impurities that is performed by the ore and by the furnace gases.

168. An electric furnace, while melting down for casting, takes 1,000 kw. and requires 400 kw. to hold the charge of 10 tons of steel at the casting temperature. The heat required to raise 1 kg. of steel to the melting point is 250 Cal.; to melt the steel, 50 Cal. Assume a uniform heat loss from the furnace throughout the operation.

The melting point of the steel is 1500°. Specific heat of the molten steel, 0.20.

The total time of the operation is 8 hr. During the time following the melting, while the charge is being deoxidized, freed from slag, and tapped, the temperature is held constant at the casting temperature, 1700°.

Required: 1. The time to heat the charge to the melting point.

2. The time to melt the charge.

3. The time to superheat the charge.

4. The electrothermal efficiency of the whole operation.

5. The total time required, and the efficiency, if 1,500 kw. is used while heating up to the melting point.

169. An electric furnace uses 20,000 amp. at 75 volts, with a power factor of 0.80. It heats 6,000 kg. of steel from 0° to its melting point of 1500° in 2 hr. When just melted, each kilogram of steel contains 290 Cal. Latent heat of fusion, 51 Cal. Specific heat of molten steel, 0.21. After melting, the steel is superheated to 1680° for casting.

Assume that the rate of heat loss during any period is proportional to the mean temperature during that period.

Required: 1. The average thermal efficiency of the furnace during the heating-up period.

2. The time required to melt the steel, and the efficiency in this period.

3. The time required to superheat, and the efficiency during this period.

170. A certain bituminous coal contains the following:

	Per Cent
C	78
H	5
O	8
Ash	8
H_2O	1

It is burned in a heating furnace for heating soft steel ingots for forging. Assume that only the theoretical quantity of air is used for combustion. The gases leave the furnace at 1000°C. Per 1,000 kg. of coal burned, 10,000 kg. of ingots is heated to 1000°C. in 1 hr.

Required: 1. The percentage of the calorific power of the coal lost to the chimney.

2. The percentage of the calorific power of the coal used for heating the ingots.

3. How much electric power would be required to heat the same ingots, assuming the same heat radiation and conduction from the furnace per hour as when burning coal?

4. How much electric power would be required merely to hold the ingots at 1000°, after they have been raised to that temperature?

171. In the first (refining) period, a basic electric steel furnace treats 10 tons of charge having an average composition as follows:

	Per Cent		Per Cent
C	2.0	P	0.8
Mn	0.8	S	0.2
Si	1.0	Fe	95.2

The finished steel (ready for superrefining) is to contain one-fourth of the original carbon, one-fifth of the original silicon, and one-half of the original manganese, but no sulphur or phosphorus. The oxidation of the impurities is accomplished by the addition of iron ore containing Fe_2O_3, 85 per cent, and SiO_2, 15. The slag made carries iron equal to 2 per cent of the total iron charged, all of it coming from the reduction of Fe_2O_3 of the ore to FeO, and 40 per cent CaO. The Mn goes to the slag as MnO, Si as SiO_2, P as P_2O_5, S as CaS, and the C oxidizes to CO.

Required: 1. The weight of ore used.

2. The weight of slag made.

3. The weight of lime used.

4. The weight of steel made.

172. An electric furnace is charged with 4 tons of steel scrap and 4 tons of pig iron. During the heat there are added 600 kg. of iron ore and enough $CaCO_3$ to make a slag of 40 per cent CaO. As deoxidizers there are used 80 kg. of ferromanganese and 36 kg. of ferrosilicon.

There is produced, ready to be superrefined, 7,960 kg. of steel analyzing C, 0.3 per cent; Mn, 0.2; Si, 0.1; P, 0.02; Fe, 99.38

The materials used analyze as follows:

	Steel scrap, per cent	Pig iron, per cent	Ferromanganese, per cent	Ferrosilicon, per cent	Iron ore, per cent
Fe	99.0	92.0	12	50	Fe_2O_3 80
C	0.5	4.0	6		
Mn	0.3	0.8	80		MnO 4
Si	0.12	1.2	2	50	SiO_2 16
P	0.08	2.0			

Required 1 A charge balance of the furnace.

2. The percentage composition of the slag

173. An electric furnace, basic-lined, produces 10 metric tons of steel from the following charge:

	Kilograms
Steel scrap	7,000
Pig iron	3,000
Lime	200

During the heat there are used as flux 1,000 kg. of mill scale and enough lime to yield a slag of 42 per cent CaO and at the end, for recarburizing and deoxidizing, 100 kg. of ferromanganese and 50 kg of ferrosilicon. Electrode consumption, 100 kg.

The finished steel contains Fe, 98.9 per cent; C, 0.6; Si, 0.2; Mn, 0.2; P, 0.07; S, 0.03.

The steel scrap contains Fe, 99.1 per cent; C, 0.4; Si, 0.15; Mn, 0.2; P, 0.08; S, 0.07.

The lime is pure CaO.

The mill scale is pure Fe_3O_4.

Ferromanganese: Fe, 13 per cent; C, 5; Si, 2; Mn, 80.

Ferrosilicon: Fe, 48 per cent; C, 2; Si, 50.

Electrodes: C, 95 per cent; SiO_2, 5.

Pig iron: Fe, 92.5 per cent; C, 4; Si, 1; Mn, 1; P, 1.3; S, 0.2.

Heat contained in the molten slag, 500 Cal. per kilogram.

Heat contained in the molten steel, 325 Cal. per kilogram.

Power used, 1,500 kw. for 5 hr.

Required: 1. The weight of lime added as flux during the heat.

2. The weight and the percentage composition of the slag.

3. The thermal efficiency of the furnace.

174. Eighteen tons of stainless steel scrap (18 per cent Cr, 8 Ni, 0.20 Si, 0.03 S) and 6 tons of bar iron, containing 0.018 per cent sulphur but no chromium, nickel, or silicon, are melted in an electric arc furnace. The slag at the end of the melting period weighs 1,000 lb. and contains 0.5 per cent FeO and 1 per cent Cr_2O_3; assume that only this iron and chromium have been taken from the original charge, the balance of the slag having been added.

Neglect oxidation of carbon from the electrodes and also any air that may enter the furnace.

Required: 1. How much ferrochromium (70 per cent Cr) and how much shot nickel (98 per cent Ni) should be added to the charge to bring the composition of the entire bath to a content of 18 per cent Cr, 8 Ni?

2. How many pounds of ferrosilicon (80 per cent Si) should be charged to reduce all the FeO in the slag to Fe and all the Cr_2O_3 to Cr and leave 0.30 per cent Si in the steel?

3. How much coke breeze (85 per cent C) would be needed to form enough CaC_2 to reduce the sulphur in the bath to 0.015 per cent, according to the reaction $3(Mn.Fe)S + 2CaO + CaC_2 = 3(Fe.Mn) + 3CaS + 2CO$, also, to reduce the FeO content of the steel from 0.27 to 0.03 per cent by reaction of FeO with CaC_2, and to leave the slag with 1.5 per cent CaC_2?

4. If 1 ton of the same charge as above were melted in an Ajax-Northrup high-frequency induction furnace, where no CaC_2 is formed, how much coke breeze (85 per cent C) would be required to desulphurize according to the reaction $CaO + (Mn.Fe)S + C = CaS + (Mn.Fe) + CO$; also, to reduce the FeO content of the steel from 0.27 to 0.03 per cent? In this case allow for a carbon content of 0.5 per cent in the slag.

CHAPTER VIII

PRODUCTION OF BLAST AND DRAFT

The use of blast and forced draft is so common in metallurgical work that it is important to be able to carry out certain calculations regarding these processes, particularly the amount of power required to furnish the blast for blast furnaces and converters.

Power Requirement for Blast

A precise calculation of power requirement depends on the method used for compression or production of draft. If compression is used, it is necessary to know to what extent the process is adiabatic or isothermal. If a fan blower is used, other considerations apply. A full discussion of this subject would take the reader far from the subject of metallurgy and would require more space than can properly be allotted to it here. It seems desirable, however, to show how the approximate requirement of power can be rapidly estimated. Two different methods will be presented, and it is a matter of much interest to note how closely the results compare, though the methods apparently differ so widely. It must be remembered that even the exact agreement which may sometimes be obtained by these two methods does not mean that the result is an exact determination of the power required, since certain refinements of method have been ignored.

The necessary data for the approximate calculations of power are simply the actual volume of air supplied per unit time (as measured at the existing conditions of temperature and barometric pressure), the pressure which the air has after compression, and the mechanical efficiency of the machine used. If these data are known, it is immaterial for an approximate result, under the conditions which usually prevail in metallurgical work, whether the process is one employing a piston compressor or a fan or a rotary blower, even though one of the two methods to be given below is based on an imaginary cylinder diagram. If the pressure of the air before compression differs from normal atmospheric pressure by an important amount, as would be the case, for example, at high altitudes, it is necessary to know also this actual barometric pressure.

The Adiabatic Formula.—The first method employs the well-known formula for work done in adiabatic compression:

$$W = \frac{k}{k-1} V_0 P_0 \left[\left(\frac{P_1}{P_0} \right)^{\frac{k-1}{k}} - 1 \right].$$

Here V_0 represents the volume of gas before compression; and if there is used not simply the volume but the volume per unit of time, the formula gives power required (at 100 per cent mechanical efficiency). k in the formula is the ratio of the specific heat of the gas at constant pressure to the specific heat at constant volume, $\frac{C_p}{C_v}$, and for air has the value 1.408. With this value of k, the formula becomes:

$$\text{Power} = 3.45 V_0 P_0 \left[\left(\frac{P_1}{P_0} \right)^{0.29} - 1 \right],$$

in which V_0 is the volume of air compressed per unit time (measured at pressure P_0); P_0 is the pressure of air before compression, and P_1 is its pressure after compression. If V_0 is in cubic feet per second and P_0 in pounds per square foot, the power is obtained in foot-pounds per second. Since the term $\frac{P_1}{P_0}$ is a ratio of pressures, the units employed in it for P_1 and P_0 are immaterial so long as they are the same for both. In using metric units, it is convenient to express V_0 in cubic meters per second and P_0 in kilograms per square meter; then the result divided by 100 gives approximately the power in kilowatts, since 1 kw. is approximately 100 kg.-m. per second. (The exact value is 102.0, and this should be used in more precise calculations.) It should be noted that V_0 is the actual volume of the uncompressed air at its initial pressure. In most cases, and in the absence of information to the contrary, it may be assumed that P_0 is 1 atm. (14.7 lb. per square inch = 10,330 kg. per square meter).

The final pressure of the air is usually stated in terms of "gage pressure"; since the pressure gage indicates the pressure *above* atmospheric pressure, the actual value to be used for P_1 is obtained by adding the atmospheric pressure to the gage pressure.

The volume of air used by the furnace cannot in general be taken for V_0. In the adiabatic formula, V_0 is the volume of air entering the cylinder of the compressor per stroke. Owing chiefly to clearance space in the cylinder, V_0 is always less than the piston displacement V_p. The piston displacement is given by the length of the stroke multiplied by the area of the piston, this area being corrected by deducting the area of the piston rod. The ratio $\frac{V_0}{V_p}$ is called the "volumetric efficiency" of the compressor and evidently must be taken into account in determining the proper value of V_0 for substitution in the formula when V_p is obtained from given dimensions. The value of the volumetric efficiency may be calculated from the amount of clearance, but this calculation will not be entered into here. Another factor to be considered in connection with the proper value of V_0 is the possibility of leakage of air between the compressor and the furnace. The term "coefficient of delivery" will here be used to express the ratio between the amount of air delivered at the furnace and the amount entering the cylinder of the compressor; the delivery coefficient thus includes the volumetric efficiency, and it will ordinarily be specified in the given data. Its value may be over 95 per cent with small clearance, certain types of valves, and tight mains; in many blowing systems, however, it is much less.

Example 18

A Bessemer converter is supplied with 22,000 cu. ft. of air per minute (measured at standard temperature and pressure) at a pressure of 24 lb gage. The air enters the cylinders of the blowing engine at 80°F. and normal atmospheric pressure. Assume a delivery coefficient of 90 per cent and the mechanical efficiency of the blowing engine 92 per cent.

Required. The power required to compress the blast.

Solution: $V_0 = \frac{22,000}{0.90} \times \frac{460 + 80}{492} = 26,800$ cu. ft. $= 760$ cu. m. per minute $=$ 12.6 cu. m. per second.

$P_1 = 24 + 14.7 = 38.7$ lb. per square inch $= \frac{38.7}{14.7}$ or 2.63 atm. Substituting in the adiabatic formula:

$$\begin{aligned}\text{Power} &= 3.45 \times 12.6 \times 1 \times 10,330 \left[\left(\frac{2.63}{1}\right)^{0.29} - 1\right] \\ &= 3.45 \times 12.6 \times 10,330 \times 0.324 \\ &= 146,000 \text{ kg.-m. per second} = \frac{146,000}{102} \text{ or } 1,430 \text{ kw.}\end{aligned}$$

$1,430 \div 0.92 = 1,550$ kw. required

The Diagrammatic Method.—While the reader must be referred to other books for the derivation of the formula used above, the underlying theory is evidently based on the expression of work as pressure × change in volume, which in turn follows from work = force × distance. The second method of solution of the above problem applies this underlying principle more directly and is based on an imaginary diagram.

The second is in reality a modification of the first method, certain factors being ignored, though the steps involved in its use are quite different. It is not permissible for high compression such as is employed in many uses of compressed air; but for the low pressures (usually less than 2 atm. gage) employed for blast furnaces and converters, it is a reasonably good approximation. Above a certain point, the higher the pressure the greater is the error involved. This method has the advantage of not requiring the use of a formula or the evaluation of such a term as the ratio of the pressures raised to the power 0.29.

Assume the piston in Fig. 4*a* at the beginning of its stroke, position *A*, the cylinder being filled with uncompressed air. In the graph below, Fig. 4*b*, the pressure in the cylinder p is plotted against the change in volume Δv of the cylinder occupied by the air at the right of the piston. At point *A*, corresponding with position *A*, Fig. 4*a*, $p = 1$ atm. and $\Delta v = 0$.

Let the piston be moved toward the right until it reaches position *B*, the cylinder remaining closed during the operation, compressing the air into the remaining space. If the temperature in the cylinder did not change, the pressure of the air in the cylinder would increase in inverse proportion to its volume, in accordance with Boyle's law. Let this increase of pressure be represented by the line *AB*, and assume that *AB* is a straight line (though actually it is curved).

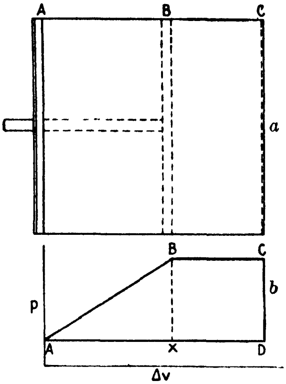

Fig. 4.

Assume that at *B* the pressure of the air has reached that at which it is desired to be delivered, P_1, and that the cylinder is now opened through a valve in such a way that the pressure of the air remains constant during the remainder of the stroke *BC* (P_1 is the total pressure, gage plus atmospheric). At the end of the stroke, uncompressed air is again admitted to the cylinder and the pressure falls again to *D* (= *A*), ready for the next stroke. The fall is here assumed vertical (*CD*), though in many compressors, depending on the type of valves, it would tend to slope in the direction of *A*.

During the stroke the work done by the piston is the product of the change in volume Δv times the pressure acting against it. This pressure is obviously neither P_0 nor P_1 but a mean between these two up to the point *B* and is P_1 during the portion *BC*. Mathematically the work done is therefore equal to the area of *ABCDA*, Fig. 4*b*. *ABCDA* is composed (under the assumptions made) of a rectangle and a triangle. The height of each (*CD*) is equal to the gage pressure, $P_1 - P_0$.

The total length *AD* is equal to the volume of the cylinder traversed by the piston in its stroke. Therefore, in order to calculate the area, it is necessary only to determine what fraction of the total stroke *AD* is represented by *BC* (= *xD* in Fig. 4*b*, the remaining fraction of the stroke *Ax* being 1 minus the fraction represented by *xD*).

Since the point *B* is reached during the stroke when the pressure has reached P_1 and since the volume is assumed to vary inversely with the pressure, $xD = \frac{P_0}{P_1}$. For example, if the final total pressure is three times the initial pressure, $xD = \frac{1}{3}$. If the pressure of the entering air is 14.2 lb. and the pressure of the compressed air 23 lb. gage, the final total pressure is 37.2 lb., and xD is $\frac{14.2}{37.2} = 0.38$. Then $Ax = 0.62$.

Example 18a

Apply this method to the data of Example 18.

As before, the volume of air before compression is 12.6 cu. m. per second. $P_0 =$ 14.7 lb. $P_1 = 38.7$ lb. The pressure of 38.7 will be reached when $\frac{14.7}{38.7}$ of the cylinder remains, so that the base of the rectangle (xD) is $\frac{14.7}{38.7}$ and of the triangle (Ax), $\frac{24}{38.7}$. The height of each is 24.

$$\text{Area of rectangle} = 24 \times \frac{14.7}{38.7} = 9.12$$

$$\text{Area of triangle} = \frac{1}{2} \times 24 \times \frac{24}{38.7} = 7.45$$

$$\text{Total} = 16.57, \text{ or } \frac{16.57}{14.7} = 1.126 \text{ atm.}$$

$$\text{Power} = 12.6 \times 1.126 \times 10{,}330 = 146{,}000 \text{ kg-m. per second} = 1{,}430 \text{ kw.}$$

$$1{,}430 \div 0.92 = 1{,}550 \text{ kw. required.}$$

It will be noted that this method corresponds to the use of an indicator diagram, in which a pressure diagram is obtained by attachment of a device to the cylinder. The graph obtained is roughly similar to Fig. 4*b* but is irregular in shape because it follows the actual pressure in the cylinder during the stroke. Its area is measured by a planimeter.

Volume of Air and Calculation of Gas Velocity.—The volume of air V_0 in the above example was obtained from the air requirement of the converter and the delivery coefficient. It may also be found from the dimensions of the cylinder and the number of strokes per minute. For example, if it is given that the cylinder is 5 ft. long and 2 ft. in diameter, the volume can be calculated. A deduction should be made for the space occupied by the piston rod. This volume multiplied by the revolutions per minute of the engine, and by 2 if double-acting, gives the volume of the air compressed per minute, neglecting clearance. To obtain the volume delivered per minute, the length of stroke must be used instead of total length of cylinder, and the result must be multiplied by the volumetric efficiency.

The volume of air delivered may also be obtained by measurement of velocity in the main at a point where the area of the cross section of the main is known or can be measured. The velocity used must be the weighted average over the entire cross-section, since the velocity varies at different points. The area in square feet multiplied by the velocity in feet per second gives the volume of air in cubic feet per second:

Volume per unit of time = area × velocity.

This method is frequently applied in metallurgical work, especially in measurements of volume of gas passing through flues, chimneys, etc. The velocity is most often determined by Pitot tube, the basic formula of which is:

$$v = \sqrt{2g\frac{h}{d}},$$

in which v is the velocity, g the acceleration of gravity, h the velocity head as read from the pressure gage used with the Pitot tube, and d is a factor for converting the velocity head to units representing the corresponding height of the air or gas whose velocity is being measured. For example, if v is being determined in feet per second, $g = 32.2$, h (usually read in inches of water) is expressed in feet of water, and d is the density of the air or gas referred to water (*i.e.*, the specific gravity, in computing which due correction must be made for the temperature and pressure of the air or gas). In using the gage, allowance may need to be made for expansion of the liquid if the surrounding temperature differs greatly from room temperature.

DRAFT

Draft is a measure of pressure and must not be confused with velocity. It is commonly expressed in inches of water or millimeters of mercury but may be expressed in any pressure units. The draft in a furnace, flue, or chimney is the difference in pressure between the inside and the outside atmosphere. In a passage containing gases in motion, the total draft is made up of the static pressure minus the velocity head due to the impact of the moving gases. If it is desired to obtain the velocity head for calculation of velocity, this is commonly done with a differential draft gage, which automatically compensates for the static pressure. The static pressure is negative with reference to the velocity head. The velocity head is the pressure required to accelerate the mass of gas and is exerted in the direction of flow.

Chimney Draft.—There is no draft in a chimney filled with air at the same temperature as the outside air and having no connection with a fan or blower. Forced draft may be produced by either pressure or suction, using a fan or blower. Natural draft is due to the difference in weight between the column of gas in the chimney and an equal column of outside air. The column of gas in the chimney and an outside column of air of equal vertical height and cross-sectional area may be thought of as though they occupied the two sides of a U tube; the cooler and therefore heavier one outside forces the lighter one inside upward with a force equal to the difference in weight between the two columns. This difference in weight may be called the *lifting power* of the gas. If the chimney were fitted with a piston, the gas in the chimney would force the piston upward, and the weight needed on the piston to keep it from being lifted would equal the above difference. In chimneys of non-uniform diameter, the lifting power is based on a column of cross-sectional area equal to that of the area of the base of the chimney. In addition to the difference in temperature between the air and the chimney gas, there is a difference in weight due to difference in composition. Although this is small, it is large enough to make it desirable to take it into consideration when the analysis of the chimney gas is known. Then the weight of the known volume of gas at its given temperature and pressure is readily computed. The pressure of the gas in the chimney, while slightly different from that of the air outside, is ordinarily sufficiently close to the barometric pressure to permit using that figure in figuring the weight of both the gas and the air. The temperature of the outside air as well as the average temperature in the chimney must be known.

The lifting power divided by the area of the base of the chimney gives the pressure per unit area, or the draft. If the lifting power is expressed in pounds and the area in square feet, the draft is then computed in pounds per square foot, which may readily be converted to inches of water or millimeters of mercury as desired.

The lifting power obviously depends on both the vertical height of the chimney and the area. The draft, on the other hand, is independent of the area, since this factor cancels out when the pressure per unit area is obtained. The draft, therefore, may be obtained without calculating the lifting power, by taking the difference in weight of the two columns each of *unit* area. If desired, the weight per unit area may be converted to inches of water or millimeters of mercury for each column before taking the difference and the draft thus directly obtained in these units.[1]

Example 19

A chimney has a diameter at the base of 10 ft. and a height of 120 ft. The gases in it analyze 75.1 per cent N_2, 5.2 O_2, 12.1 CO_2, 7 6 H_2O. The average temperature in the chimney is 350°C. The outside temperature is 16°C and barometer 748 mm.

Required: 1. The total lifting power of the chimney gases.

2. The chimney draft (*a*) in pounds per square inch and (*b*) in inches of water.

Solution: First find the weight of 1 cu. ft. of the gas, at standard conditions. This is found to be 1.32 oz.

The volume of gas in the chimney $= \pi \times 25 \times 120 = 9{,}425$ cu. ft.

At 350°C., 748 mm., this weighs $\frac{273}{623} \times \frac{748}{760} \times 9{,}425 \times \frac{1.32}{16} = 336$ lb.

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[1] The author is indebted to Prof. Alfred Stansfield, McGill University, for suggesting this direct method.

At 16°C., 748 mm., the weight of 9,425 cu. ft. of air (assumed dry) is $\frac{273}{289} \times \frac{748}{760} \times 9{,}425 \times 0.0807 = 708$ lb.

Lifting power of gases = 708 − 336 = 372 lb. (1).

Area of chimney section = 25π = 78.6 sq. ft.

$$\text{Draft} = \frac{372}{78.6} = 4.74 \text{ lb. per square foot} = 0.033 \text{ lb. per square inch (2).}$$

Atmospheric pressure = 33.9 ft. of water.

$$\text{Draft} = \frac{0.033}{14.7} \times 33.9 \times 12 = 0.91 \text{ in. of water (2).}$$

Chimney Head.—Since a pressure per unit area can be expressed as the height of a column of liquid, the draft of a chimney is equivalent to its head, *head* being the height of a column of liquid (or gas) equal to a given pressure. In the case of chimneys and flue systems, the head is usually expressed in feet of air measured at standard conditions.

The head in feet of air may be converted to inches of water by multiplying by the factor (12 × 0.001293), or 0.01552, the figure 0.001293 being the weight of air at standard conditions in grams per cubic centimeter. Conversely, the draft in inches of water may be changed to head in feet of air by dividing by 0.01552.

The total head of a chimney through which gas is moving is made up of the above pressure head minus a small velocity head minus a loss of head due to friction. Though the main component of draft is independent of the diameter of the passage, the friction loss is proportionately greater the smaller the diameter. Friction also increases rapidly with the height of the chimney and thus limits the extent to which the draft can be increased by increasing the height. This loss also becomes great when baffles or other obstructions are placed in flues. In calculations it can only be allowed for empirically.

Use of Pitot Tubes.—In using Pitot tubes, it should be noted that the value of h in the formula $v = \sqrt{2g\frac{h}{d}}$ is not uniform over the cross section of the chimney. It is customary in a relatively small passage to place the tubes a fixed distance, often one-third of the way, in from the edge, or in a relatively large passage to take several readings at different points.

Empirical coefficients are often worked out for correction of Pitot-tube readings. It might be supposed that the velocity of gases would be greatest at the center of a chimney; but, on the contrary, it is often lower here than near the edge, owing to the fact that the gases rise spirally instead of straight up.

Chimney Power and Efficiency.—The lifting power of the gas multiplied by the height of the chimney will give the equivalent of work done by the gases (in foot-pounds, for example); if the volume of gas passing per unit of time is known, there is obtained the rate of work done, or power of the chimney. This may be compared with the energy equivalent of the heat content of the gases to obtain the thermomechanical efficiency of the chimney. This value is always very low.

Problems

175. The gas from an iron blast furnace analyzes:

	Per Cent		Per Cent
CO	26	CH_4	1
CO_2	10	H_2O	2
H_2	2	N_2	59

The furnace makes 400 tons of pig iron per day and 3,900 cu. m. of gas per ton of pig iron. The blast is preheated to 600°C. in stoves having an efficiency of 65 per cent. The surplus gas is used in gas engines at a thermomechanical efficiency of 25 per cent. The blast is compressed to 1 atm. gage at an efficiency of 85 per cent

Required: 1. The percentage of the gas required by the stoves

2 The power used in compressing the blast

3. The surplus power available after supplying the stoves and blowing engines, in kilowatts.

176. An iron blast furnace, making 1,020 short tons of pig iron per day, uses 92,400 cu. ft. (standard conditions) of blast per ton of pig iron and makes gas analyzing:

	Per Cent
CO	23.8
CO_2	13.3
H_2O	1.3
H_2	2.5
N_2	59.1

The furnace uses per ton of pig iron 1,760 lb. of coke that is 87 per cent C. The pig is 3.5 per cent C

The blast is preheated to 700°C., the stoves having a thermal efficiency of 68 per cent The surplus gas is used in gas engines having 24 per cent thermomechanical efficiency. The blast pressure is 19 lb. per square inch gage. The blowing engines have an efficiency of 90 per cent

Required: 1 The cubic feet of gas made, per ton of pig iron

2. The pounds of $CaCO_3$ used, per ton of pig iron.

3 The percentage of the carbon of the coke that is burned at the tuyères, and the percentage used in direct reduction above the tuyères.

4. The percentage of the heating value of the coke that is developed in the furnace.

5. The percentage of the blast-furnace gas that is required by the stoves.

6. The power generated in the gas engines.

7 The power required to compress the blast, calculated (*a*) from the adiabatic formula, (*b*) from the theoretical indicator diagram.

177. The blast furnace of Prob. 111 uses a blast pressure of 1 atm. (gage pressure), has a capacity of 600 long tons per day, and is 120 ft. high above the skip pit. The blast is preheated to 540°C. The thermal efficiency of the stoves is 70 per cent. Surplus gas is converted into power in gas engines of 25 per cent thermomechanical efficiency.

Required: 1. The power required to supply the blast (use both adiabatic and diagrammatic methods).

2. The percentage of the gas required to furnish the power for the blast.

3. The percentage of the gas used in the stoves.

4. The power that can be generated from the remaining gas.

5. The power required to hoist the solid charge to the top of the furnace.

178. An iron blast furnace produces 720 metric tons of pig iron per day and makes per ton 4,084 cu. m. of gas analyzing CO 24.7 per cent, CO_2 14.3, H_2 0.5, N_2 60.5.

Part of this gas is used in stoves that heat the blast from 0 to 750°C. at a thermal efficiency of 65 per cent. The blast is used at a gage pressure of 20 lb. per square inch.

The rest of the gas is used in gas engines to furnish power for the blowing engines and to run electric generators. The blowing engines have a thermomechanical efficiency of 90 per cent and 85 per cent volume delivery efficiency, the generators operate at 92 per cent efficiency, and the gas engines at 25 per cent efficiency.

Required: 1. The proportion of the gas which must be sent to the stoves

2. The proportion of the gas necessary to run the gas blowing engines.

3. The power available from the generators.

179. An iron blast furnace makes 880 metric tons of pig iron per day and consumes per ton of pig iron 1,640 kg. of ore, 920 kg. of coke, and 260 kg. of $CaCO_3$. The coke is 88 per cent carbon. The pig iron is 3.6 per cent carbon.

The blast-furnace gas is composed as follows:

	Per Cent
CO	24.7
CO_2	14.3
CH_4	0.5
N_2	60 5

The blast is preheated to 650°C., in stoves having a thermal efficiency of 62 per cent.

The gas not required by the stoves is used for power production in gas engines having a thermomechanical efficiency of 23 per cent. The gas engines drive the blowing engines, which supply the blast to the furnace, and electric generators, which produce additional power. The blowing engines operate at 90 per cent mechanical efficiency, and the air-delivery coefficient is 94 per cent. The generators have 92 per cent efficiency.

The blast pressure is 22 lb. gage.

The charge is hoisted to the top of the furnace by automatic skip, operated electrically at 75 per cent efficiency; height of lift, 25 m. Assume that the hoist is running one-fourth of the time.

Required: 1. The volume of the gas and of the blast, per ton of pig iron

2. The proportion of the total gas required by the stoves.

3. The power produced by the gas engines.

4. The power required to run the blowing engines, as calculated from the theoretical indicator diagram and from the adiabatic formula.

5. The power required for the hoist.

6. The surplus power, and the net consumption of coke per ton of pig iron after crediting this surplus power to the furnace.

180. A Bessemer converter is charged with 18 long tons of pig iron of the following composition:

	Per Cent
Fe	93.2
C	3.6
Si	1 8
Mn	1 4

The blow oxidizes all the impurities, and in addition 1,200 lb. of Fe is oxidized in the second period. Two-thirds of the carbon goes to CO, and one-third to CO_2.

The blowing engines supply air at the rate of 17,000 cu. ft. per minute, measured at standard conditions The blast is delivered at 2 atm. gage pressure

Required: 1. The volume of air, at standard conditions, necessary to blow the charge.

2. The time of each period of the blow.

3 The percentage composition of the slag and gases.

4 The power required to run the blowing engine, assuming efficiency of 80 per cent

181. An acid-lined Bessemer converter blows 20 metric tons of pig iron to practically pure iron. The pig iron contained 3.6 per cent C, 1.4 Si, 1 Mn, 94 Fe The amount of Fe oxidized is 2.8 per cent of the pig; three-fourths of the carbon goes to CO, and one-fourth to CO_2

The blast pressure (gage) is 25,000 kg. per square meter The blowing engine makes 50 r p m and is double-acting. The internal diameter of the cylinder is 1.6 m., and the length of the stroke 2 m. The piston rod is 15 cm in diameter and extends through both ends of the cylinder. The mechanical efficiency of the engine is 92 per cent, and the efficiency of the air delivery is 88 per cent.

Required. 1. The total volume of air, at standard conditions, necessary for the blow.

2 The time required, by periods

3. The volume and percentage composition of the gases in each period

4. The power required for the blowing engine

182. A 10-ton charge of pig iron in a Bessemer converter gave a slag analyzing FeO, 31.2 per cent, SiO_2, 43 4; MnO, 25.4 The slag weighed 915 kg , including 183 kg. of SiO_2 taken up from the lining of the converter. The gases from the converter amount to 3,190 cu m , measured at standard conditions, and analyze CO, 16 2 per cent; CO_2, 7 0; N_2, 76 8. The blast is delivered at 1.8 atm. gage pressure. The time of the blow is 12 min

Required· 1. The percentage composition of the pig iron used in the converter.

2. The cubic meters of air required for the blow. (Calculate by both oxygen and nitrogen methods.)

3. If the temperature at which the above volume of gas was measured was 27°C. and the barometer 740 mm , instead of standard conditions, how much steam (kilograms per cubic meter of air) could be added to the blast and the time of the blow be unchanged?

4. The power required of the blowing engine, assuming 88 per cent efficiency

183. A basic-lined Bessemer converter receives 20 short tons of the following pig iron:

	Per Cent		Per Cent
C	3 05	S	0.33
Mn	0.41	P	1 37
Si	0.83	Fe	94 01

At the end of the blow the bath contains 0.17 per cent C, 0.10 Mn, 0.055 S, 0.06 P, 0 Si and totals 37,000 lb.

The carbon forms CO and CO_2 in the proportion 4:1. Assume that oxidation of iron is confined to the second and third periods and is divided between them in proportion to their lengths. Sulphur is removed entirely as CaS; the gases contain no O_2 or SO_2.

During the blow, 1,200 lb. of burned dolomite (assume CaO.MgO) is corroded from the lining; and, in addition, enough pure CaO is added to make a slag of 67 per cent CaO

The blowing engines deliver air at 26 lb. per square inch gage pressure, with a coefficient of delivery of 94 per cent and a mechanical efficiency of 92 per cent. The engines are double-acting, 90 r.p.m.; internal diameter of cylinder 3.6 ft., length of stroke 6.6 ft. The piston rod (through both sides) has a diameter of 6 in.

Required: 1. The total volume of air used for the blow.

2. The time of each period of the blow.

3. The percentage elimination of the various impurities and percentage loss of iron.

4. The weight of lime added and of slag produced.

5. The value of the steel at 1.8 cts. per pound and of the Thomas slag at $1.10 per unit of calcium phosphate [$Ca_3(PO_4)_2$] contained

6. The power required to run the blowing engines, as calculated from the theoretical indicator diagram.

184. A basic-lined Bessemer converter blows 15 tons of pig iron containing:

	Per Cent
C	3.6
Mn	0.9
Si	0.7
P	2.2

3.6 per cent Fe is also oxidized, this being distributed uniformly throughout the blow. Three-fourths of the carbon goes to CO, one-fourth to CO_2. Enough lime (CaO) is added to make a slag of 10 per cent SiO_2.

The pressure of the blast is 1.7 atm. gage. The blowing engine makes 90 r.p.m. The internal diameter of the cylinder is 1.0 m., the length of the stroke 2 m. The engine is double-acting. The piston rod (through both sides) has a diameter of 15 cm. The mechanical efficiency of the engine is 92 per cent, and the coefficient of delivery of the air is 88 per cent.

Required: 1. The total volume of air used for the blow, at standard conditions

2. The time of the blow by periods.

3. The weight of lime added

4. The power required for the blowing engine.

5. The total blowing time if 0.02 kg. of steam per cubic meter of air were blown in, to limit the temperature rise in the converter.

185. The stack in a smelting plant is 400 ft. high. Its inside diameter is 35 ft. at the base and 24 ft. at a point about one-third of the way up, where Pitot tubes are inserted for measurement of the draft and velocity head. For this measurement the cross section at this point is regarded as being divided into six concentric circular rings having radii of 2, 4, 6, 8, 10, and 12 ft. The average velocity head in each of these was found to be 0.031,0.042, 0.042, 0.040, 0.038, and 0.034 in. of water, respectively. The temperature of the gases at this point, which was also the average temperature of the gases in the stack, was 160°C., and the pressure 740 mm. The temperature of the outside air was 20°C. The composition of the gases was CO_2, 12 per cent; SO_2, 1; O_2, 8; H_2O, 2; N_2, 77.

Required: 1. The total lifting power of the stack gases, in pounds.

2. The stack draft, in pounds per square inch and in inches of water.

3. The maximum velocity in the stack at the 24-ft. section as calculated from the velocity head of 0.042 in., in feet per minute

4. The total volume of gases passing through the stack in 24 hr., measured at the given conditions.

186. A producer gas analyzes:

	Per Cent
CO	27
CO_2	3
CH_4	2
H_2	6
N_2	62

It is used in a furnace with 20 per cent excess air. The flue gases leave the furnace at a temperature of 377°C. and the stack at 327°. Atmospheric temperature, −10°, barometer, 765 mm The gas is burned at the rate of 1 cu. m. per second. The chimney has a uniform diameter of 1 m. and a height of 20 m.

Required: 1. The velocity of the flue gases at the bottom and top of the chimney

2. The total lifting power of the chimney gases, in kilograms.

3. The chimney draft, in centimeters and in inches of water.

4. The total head of the chimney, in meters and feet of air at standard conditions.

5. The thermomechanical efficiency of the chimney.

187. A producer gas, when burned at the rate of 1 cu. m per second with 10 per cent excess air, both air and gas being preheated to 1000°C , gave, per cubic meter of gas burned, a flue gas containing the following: CO_2, 0 31 cu. m.; H_2O, 0.18, O_2, 0.02; N_2, 1.44. The calorific intensity was 2090° The calorific power of the gas was 1,145 Cal. per cubic meter. The heat in the preheated gas was 358 Cal and in the air, 365 Cal.

Temperature measurements in the furnace gave the following results.

At the flame end, 1900°C
At the flue end, 1650
Leaving the checkers and entering the waste-heat boiler, 750.
Leaving the boiler and entering the stack, 350
Leaving the stack, 250

The stack was 50 m. high and had a uniform cross-sectional area of 1 sq. m. The velocity of the gases in the stack was 5 m per second

Required 1 The percentage of the total heat entering the furnace that is:

a Lost in combustion
b. Used in the furnace
c. Extracted in the checkers.
d. Extracted in the boiler.
e. Lost from the stack.

2 The percentage efficiency of the checkers.

3. The percentage of the heat entering the checkers that is retained by them.

4. The draft in the stack, in millimeters of mercury.

5. The thermomechanical efficiency of the stack

CHAPTER IX

THE HEAT BALANCE

The heat balance is an extremely useful calculation in nearly all kinds of furnace operations. It has been widely employed in the design of furnaces and processes for the purpose of estimating fuel requirements and also in the determination of furnace efficiencies and general thermal study of processes.

A heat balance consists of a listing and evaluation of all items of heat supplied or available and a similar listing and evaluation of heat used, lost, or distributed, the sum of the first set of items being equal to the sum of the second set. In practice it is usually not possible to evaluate all items. In most cases the heat lost by radiation, convection, and conduction to the ground or supports cannot be determined directly; but all other items of important magnitude may be determined, and the difference between the total heat supplied and the determined amount of heat distributed is then called heat lost by radiation, convection, and conduction, the two sides being thus caused to balance. In other cases it may be possible from a prior knowledge of similar furnaces or processes to estimate fairly closely the amount of heat that would be lost by radiation, convection, and conduction, and this estimate may be entered in the balance sheet to afford a determination by difference of some other unknown item. This procedure is followed in estimating the quantity of heat to be supplied by fuel when the fuel requirements are sought. In such cases it must be borne in mind that the accuracy of the determination of the fuel requirement depends in large measure on the accuracy of the estimate of heat loss by radiation, etc. There is danger of overconfidence in the results of such a calculation, an overconfidence which may be enhanced by the fact that some of the items of the balance sheet may be determined very closely. In reality, when quantities are to be determined by difference it is the old question of the chain being no stronger than its weakest link. The author knows of one published determination of this kind in which the quantity of heat calculated by difference was less than 1 per cent of the total quantity of heat involved in the balance, whereas the probable error in some of the items amounted to several per cent of the total.

Items of Heat Supply.—The sources of heat supply and the points of distribution vary in different processes. In general the sources of heat entering may include the following:

1. Heat of combustion of the fuel (or in electric furnaces the electrical energy input)
2. Sensible heat in the fuel (usually small enough to be negligible except in preheated gas).
3. Sensible heat in the air supplied (often negligible).
4. Sensible heat in the furnace charge (usually negligible)
5. Heat developed by exothermic reactions in the furnace

Items of Heat Distribution.—In general the items of heat leaving may include the following:

1. Heat consumed in endothermic reactions in the furnace
2. Heat used in evaporation of moisture
3. Sensible heat in the hot flue gases
4. Sensible heat in the principal furnace product, *e.g.*, metal or matte
5. Sensible heat in the slag
6. Heat absorbed by cooling water.
7. Heat lost by radiation to surroundings
8. Heat lost by convection to air in contact with furnace.
9. Heat lost by conduction to the ground or furnace supports. (Since the heat lost by radiation and convection must first pass through the walls of the furnace, items 7, 8, and 9 may be included in the single item of "heat lost by conduction through the furnace walls" This, however, would not include heat lost through open doors or other openings in the furnace.)

Since the chemical reactions in a furnace during any particular stage of the process are not separate and distinct but occur for the most part simultaneously and interdependently, it is usually desirable to combine item 5 of heat supply and item 1 of heat distribution, obtaining thus the "net heat of reaction," which is then entered on the appropriate side of the balance sheet depending on whether the net amount is generated or absorbed.

HEAT BALANCE OF THE IRON BLAST FURNACE

As an example of a thermal balance sheet, one will be worked out for the iron blast furnace for which a charge balance sheet has already been set up on page 111. Since the charge balance was worked in pounds, the pound-calorie will be adopted as the heat unit in this example.[1] In the statement of the example below, the data given on page 109 are repeated and the necessary thermal data added.

Example 20

An iron blast furnace smelting a magnetite ore uses per day 912 short tons of ore, 510 tons of coke, and enough limestone to yield a slag of 40 per cent SiO_2. Assume that all of the phosphorus, one-half of the manganese, and one-fifth of the silicon charged are reduced and go into the pig iron, which also contains by analysis 4 per cent carbon. Assume all the sulphur slagged as CaS. 1 per cent of the iron charged is lost in the slag. The blast amounts to 112,000 cu. ft. (measured at 60°F., 30 in. pressure) containing 9 grains of moisture per cubic foot, per ton of coke charged.

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[1] To convert pound-calories to B.t.u., multiply by 1.8.

The analyses of the ore, flux, and coke are as follows:

Ore, per cent		Flux, per cent		Coke, per cent	
Fe_3O_4	70.3	$CaCO_3$	95.4	C	87.2
Fe_2O_3	4.8	$MgCO_3$	2.5	SiO_2	9.0
SiO_2	10.2	Al_2O_3	0 5	FeS	2 0
P_2O_5	0.9	SiO_2	0.9	H_2O	1 8
MnO_2	3 6	H_2O	0 7		
Al_2O_3	2.6				
H_2O	7.6				

The blast is preheated to 1100°F. The gas leaves the top of the furnace at 400°F. The pig iron and the slag are tapped at 2900°F. The furnace uses per day 400,000 gal. of cooling water, which enters at an average temperature of 50°F. and leaves at an average temperature of 150°F.

Required: A heat balance of the furnace.

Solution: The amounts of the various items of heat supply and distribution will be calculated first, and then they will be summarized in the form of a balance sheet. The amounts will be calculated in pound-calories per day divided by 1,000, to agree with the quantities in the charge balance sheet (page 111) This means that the amounts will be calculated per 0 912 short ton of ore charged or per 1,091 lb of pig iron produced.

1. *Heat Derived from Combustion of the Coke.*—The statement of the problem shows that the amount of coke used was 0.51 ton, or 1,020 lb., containing 890 lb. of carbon. From this must be deducted the carbon entering the pig iron; the remaining carbon is oxidized. It is first necessary to calculate how much of the carbon goes to CO and how much to CO_2. This has already been done, in part, in connection with the charge balance sheet. We shall take the results from the previous calculation, shown on page 112, and shall likewise take whatever previously calculated figures are necessary during the remainder of the example. We have:

$$\text{C to CO} = \tfrac{12}{28} \times 1{,}323 = 566 \text{ lb.}$$
$$\text{C to CO}_2 = 846 - 566 = 280 \text{ lb.}$$

It is true that not all this oxidation of carbon represents "combustion" by the blast. Some is due to reduction of oxides and accompanying oxidation of carbon or CO. But the balance sheet is here being calculated with reference to the furnace as a whole, and there is no need of dividing the oxidation in this manner. Counting all the oxidation of carbon as combustion, we have:

Heat generated by $C \rightarrow CO$: $566 \times 2{,}430 = 1{,}375{,}000$ lb.-cal.
Heat generated by $C \rightarrow CO_2$: $280 \times 8{,}100 = \underline{2{,}268{,}000}$
$3{,}643{,}000$ lb.-cal.

In the charge balance it was assumed that the FeS of the coke was not oxidized. Hence, heat from this will be neglected. The decomposition of the FeS and slagging of the sulphur as CaS will be entered under the head of chemical reactions. Evaporation of the moisture of the coke will be included with moisture of the ore.

2. *Sensible Heat in the Charge.*—Since the charge is not pre-heated, this item is very small compared with the others and hence may be neglected.

3. *Sensible Heat in the Blast.*—The blast amounted to 4,300 lb. of dry air and 73 lb. of H_2O. The temperature was 1100°F. (= 593°C.). Using the specific heat in pound-calories per pound, given in Table XV, page 393, we have:

$$\begin{array}{lrl} \text{In dry air:} & 4{,}300(0.234 + 0.0000173 \times 593)593 = & 623{,}000 \text{ lb.-cal} \\ \text{In } H_2O\cdot & 73(0.46 + 0.00006 \times 593)593 = & \underline{21{,}000} \\ & & 644{,}000 \text{ lb.-cal} \end{array}$$

4. *Heat of Formation of the Slag.*—An inspection of the percentage composition of the slag shows it to be composed of about 40 per cent SiO_2 and 9 per cent Al_2O_3 and the remainder chiefly bases, mostly CaO. Its formation, therefore, approximates the formation of the compound $CaO.SiO_2$ (the molecular weights of CaO and SiO_2 being nearly equal) with some further combination with Al_2O_3. Table XLIV, page 417, gives the heat of formation of $CaO.SiO_2$ as 420 lb.-cal. per pound of SiO_2. The effect of the Al_2O_3 is uncertain and probably small. If the heat of formation of the slag is taken as 420 lb.-cal. per pound of SiO_2, we have:

$$226 \times 420 = 95{,}000 \text{ lb.-cal}$$

This is perhaps the best estimate that can be made of the heat of formation of the slag. Although this figure is based on assumption and may in itself contain an error of 25 per cent or more, it is a relatively small item in the entire heat balance.

This completes the items of heat supplied.

5. *Heat of Formation of the Pig Iron from Its Constituents.*—Since molten pig iron is a solution of several elements in iron, evidently some heat of formation is involved in the combination of the elements. A principal item in the combination would be the formation of Fe_3C. Table XXIX, page 405, gives this heat of formation as $-5{,}200$ cal. per formula weight, or -433 cal. per unit weight of carbon.

$$44 \times (-433) = -19{,}000 \text{ lb.-cal.}$$

The heat of formation of Fe_3Si is $-20{,}000$ cal. The solution of the silicon may therefore absorb additional heat:

$$26 \times \frac{-20{,}000}{28} = -19{,}000 \text{ lb.-cal.}$$

The effect of the manganese and phosphorus appears to be small, and it is probably best to neglect these in the absence of more information.

The above indicates that 38,000 cal. is *required* to form the pig iron. tem 5 may therefore be included with the items of heat distributed. Evidently the exact value and even the algebraic sign of item 5 are somewhat uncertain, but it is entirely certain that the magnitude is very small. Though of unimportant magnitude, it may be included in the balance sheet for the sake of completeness.

6. *Heat Absorbed in Reduction of Oxides.*—Using the weights of elements reduced and entering the pig iron as shown in the balance sheet, and multiplying each by the heat of formation per unit weight of metal as given in Table XLII, page 414:

(*a*) $Fe_3O_4 \rightarrow Fe$: $928 \times 1,588 = 1,472,000$ lb.-cal.
(*b*) $Fe_2O_3 \rightarrow Fe$: $52 \times 1,777 = 92,000$.
(*c*) $SiO_2 \rightarrow Si$: $26 \times 7,160 = 186,000$.
(*d*) $P_2O_5 \rightarrow P$: $7 \times 5,912 = 41,000$.
(*e*) $MnO_2 \rightarrow Mn$: $21 \times 2,239 = 47,000$.

In addition, some Fe_2O_3 is reduced to FeO only, forming 13 lb. of FeO n the slag, and some MnO_2 is reduced to MnO, forming 27 lb. of MnO in the slag. The FeO contains $\frac{56}{72} \times 13 = 10$ lb. of Fe. The reduction of Fe_2O_3 to FeO is equivalent to reduction to Fe followed by reoxidation to FeO; the heat absorbed is therefore $1,777 - 1,151 = 626$ lb.-cal. per pound of Fe.

(*f*) $10 \times 626 = 6,000$ lb.-cal.

Similarly, for MnO, $\frac{55}{71} \times 27 = 21$ lb. of Mn.

(*g*) $21(2,239 - 1,757) = 10,000$ lb.-cal.

By adding items (*a*) to (*g*), the total heat absorbed in reduction of oxides is found to be 1,854,000 lb.-cal.

7. *Heat Absorbed in Decomposition of* $CaCO_3$ *and* $MgCO_3$.—Four hundred and twenty-nine pounds of $CaCO_3$ and 11 lb. of $MgCO_3$ are decomposed to CaO and MgO. Multiplying by the heats of formation per unit weight of compound, from Table XXX, page 406:

$$\begin{array}{rl} 429 \times \frac{43,450}{100} = & 186,000 \text{ lb.-cal.} \\ 11 \times \frac{27,800}{84} = & \underline{4,000} \\ & 190,000 \text{ lb.-cal.} \end{array}$$

8. *Heat Absorbed in Decomposition of* FeS *and Formation of* CaS *from* CaO.—Since FeS and CaO are decomposed and CaS is formed, the net heat absorbed by the reaction (omitting the part played by carbon and

CO, which has already been included in item 1) is given by the sum of the heats of formation of FeS and CaO minus the heat of formation of CaS. Per formula weight:

$$23{,}100 + 151{,}600 - 113{,}500 = 61{,}200 \text{ cal.},$$

equivalent to $\frac{61{,}200}{32}$, or 1,910 lb.-cal. per pound of S.

$$7 \times 1{,}910 = 14{,}000 \text{ lb.-cal.}$$

9. *Heat Absorbed in Evaporation of* H_2O.—The total water evaporated is:

$$\begin{aligned} 138 + 3 + 18 &= 159 \text{ lb} \\ 159 \times 586 &= 93{,}000 \text{ lb.-cal.} \end{aligned}$$

10. *Heat Absorbed in Decomposition of* H_2O *in the Blast.*—Moisture in the blast comes in contact with white-hot carbon and is consequently decomposed as soon as it enters the furnace. The heat gained by oxidation of carbon in this manner has been included in item 1. The heat of decomposition of $H_2O \rightarrow H$ is therefore to be figured here. The amount of H_2O decomposed is 73 lb.

$$73 \times \frac{57{,}840}{18} = 235{,}000 \text{ lb.-cal.}$$

11. *Sensible Heat in the Blast-furnace Gas.*—The temperature is 400°F. (= 204°C.). Taking the weights of the different gases shown on page 112 and the specific heats by weight from Table XV, page 393:

Heat content of:

$$\begin{aligned} CO &= 1{,}323(0.242 + 0.000018 \times 204)204 = 66{,}000 \text{ lb.-cal.} \\ CO_2 &= 1{,}218(0.205 + 0.000046 \times 204)204 = 53{,}000 \\ H_2O &= 159(0.46 + 0.00006 \times 204)204 = 15{,}000 \\ H &= 8(3.35 + 0.00022 \times 204)204 = 6{,}000 \\ N &= 3{,}302(0.241 + 0.000018 \times 204)204 = 165{,}000 \\ &\text{Total} = 305{,}000 \text{ lb.-cal.} \end{aligned}$$

12. *Sensible Heat in Molten Pig Iron.*—Table XVII, page 395 gives the heat content of molten pig iron at its melting point (1100°C.) as 230 lb.-cal. per pound; to this must be added the heat required to superheat the metal to 2900°F. (1593°C.). The specific heat of molten pig iron containing 4.0 per cent carbon is about 0.15 (Table XVII).

$$1{,}091(230 + 493 \times 0.15) = 332{,}000 \text{ lb.-cal.}$$

This item and the one following both involve some uncertainty due to lack of knowledge of the exact values of heat contents and specific heats of pig iron and slag of varying compositions.

13. *Sensible Heat in the Slag.*—Figures for the heat contents of slags are uncertain because the analyses of slags differ. A fair approximation,

however, is obtainable from Table XIX, page 398, which gives the heat content of a slag similar to the one in this problem as 400 cal. at the melting point of 1300°C. and the specific heat of liquid slag as about 0.30. The total heat content of the slag per pound would then be $400 + 300 \times 0.30 = 490$ lb.-cal.

$$563 \times 490 = 276{,}000 \text{ lb.-cal.}$$

It may be noted that available data indicate that a considerable variation in slag composition does not cause an extremely large difference in total heat content at a given temperature.

14. *Heat Absorbed by Cooling Water.*—400,000 gal. of water per day $\div$ 1,000 = 400 gal. $400 \times 3.785 = 1{,}514$ liters = 1,514 kg. $\times$ 2.205 = 3,340 lb. This is raised 100°F., or 55.6°C.

$$3{,}340 \times 55.6 = 186{,}000 \text{ lb.-cal.}$$

15. *Heat Lost by Radiation, Convection, and Conduction.*—No data being available for calculation of this item, it will be assumed to make up the difference between the sum of the items of heat supplied and the sum of the other items of heat distributed. This is 4,371,000 − 3,523,000 = 848,000 lb.-cal.

SUMMARY—HEAT BALANCE SHEET OF IRON BLAST FURNACE

Heat supplied	Pound-calories	Per cent	Heat distributed	Pound-calories	Per cent
Combustion of coke	3,643,000	83.3	Formation of pig iron	38,000	0.9
Heat in blast	644,000	14.8	Reduction of oxides	1,854,000	42.4
Formation of slag	84,000	1.9	Decomposition of carbonates	190,000	4.3
			FeS → CaS	14,000	0.3
			Evaporation of H_2O	93,000	2.1
			Decomposition of H_2O	235,000	5.4
			Heat in blast-furnace gases	305,000	7.0
			Heat in pig iron	332,000	7.6
			Heat in slag	276,000	6.3
			Heat in cooling water	186,000	4.3
			Loss by radiation, etc	848,000	19.4
Total	4,371,000	100.0	Total	4,371,000	100.1

NOTES: It is observed in the above balance sheet that the heat available for supplying the losses by radiation, convection, and conduction (848,000 lb.-cal.) is only a little more than the heat derived from the sensible heat in the blast. This indicates the necessity of heating the blast; while it does not prove conclusively that the furnace would freeze if operated with cold blast, because the whole operation of the furnace would change, altering the other items of the balance sheet also, it points strongly to that conclusion.

This quantity also amounts to about one-fifth of the heat derived from combustion of coke, indicating a considerable deficiency of heat if the coke charged were reduced to four-fifths of the amount used, *i.e.*, to 408 tons instead of 510. In fact, if the heat balance of the furnace is calculated with a reduction in coke of considerably *less* than one-fifth and a corresponding reduction in the amount of blast, the sum of the items of heat distributed without including the item of loss by radiation, etc., is *greater* than the heat supplied. This indicates the close adjustment of coke necessary in the modern blast furnace.

The amount of heat absorbed by cooling water is a very small part of the total. This is normal. The cooling water merely removes excess heat from certain points where it would cause damage. In the water-jacketed copper or lead blast furnace we should expect this item to be larger and the loss by radiation, etc., smaller

The heat which passes out when the furnace is tapped, *i.e.*, the sensible heat in the outflowing slag and pig iron, amounts here to about one-sixth of the total heat.

The loss of heat in the gases is very small in the iron blast furnace because the heat is taken up by the charge as the gases rise through the shaft. The gases leave at a low temperature In the open-hearth furnace (see page 136) the heat contained in the gases leaving the furnace proper is 65 per cent of the total heat supplied, instead of 7 per cent as here in the blast furnace.

As a check on the reasonableness of the amount of heat lost by radiation, etc., this may be compared with results for other furnaces. Richards[1] states that the loss by conduction may vary between 60 and 200 cal per unit of pig iron, and quotes Bell as using 169 cal. for a Cleveland blast furnace.

The sum of conduction, convection, and radiation loss, Richards says, is usually between 100 and 500 cal per unit of pig iron and would be near the larger figure for a modern coke furnace. In the balance sheet above, this loss is 848,000 lb-cal for 1,091 lb. of pig iron, or 777 cal per unit This is a high value, an indication perhaps that the coke consumption could be somewhat reduced. The amount of this loss, however, depends more on the construction of the furnace than on the amount of coke used.

Thermal Efficiency of the Iron Blast Furnace.—If the main function of the blast furnace be considered as the reduction of the iron oxide to iron and the efficiency be calculated from the amount of heat utilized in doing this, divided by the total heat available, the efficiency of the above furnace would be $\frac{1,564,000}{4,371,000}$, or 36 per cent. A better expression of efficiency, however, is derived from considering that the useful work of the furnace is the carrying on of *all* the chemical reactions necessary to make the pig iron, including the necessary making of slag, and also heating the pig iron and slag to the temperatures required to separate them and remove them from the furnace. This includes all the items of heat distribution except those which are clearly non-useful losses, *viz.*, the sensible heat in the outgoing gas, the heat in the cooling water, the loss by radiation, etc. On this basis the efficiency of the above furnace is $\frac{3,032,000}{4,371,000}$, or 69 per cent.

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[1] "Metallurgical Calculations," p. 289, McGraw-Hill Book Company, Inc., New York, 1918.

Still another type of efficiency which may be evaluated in a blast furnace is that obtained by dividing the useful heat, not by the heat actually supplied, but by the total potential calorific power of the coke plus the heat in the blast. The calorific power of the coke in the above example is 890 × 8,100 = 7,209,000 lb.-cal. Adding the 644,000 lb.-cal. in the blast gives 7,853,000 lb.-cal This thermal efficiency then is $\frac{3,032,000}{7,853,000}$, or 39 per cent.

HEAT BALANCE OF BESSEMER CONVERTER AND OPEN-HEARTH FURNACE

The heat balance of the Bessemer converter is much simpler than that of the blast furnace. No fuel is used and the blast is not preheated, all the heat being derived from oxidation of various elements and formation of the slag. The distribution of heat is also simpler.

In the open-hearth furnace, fuel is the main source of heat; but preheated air, and in some furnaces preheated fuel gas also, contribute heat, and some heat is derived from chemical reactions in the charge The losses by radiation, etc., are relatively much greater than in the blast furnace or Bessemer converter. No special discussion of the procedure for calculation of the heat balance is necessary. The results of a calculation of this kind are illustrated in the following tabulation;[1] as in the case of the blast furnace, variations in the method of accounting may be made in the case of some of the items.

TYPICAL HEAT BALANCE OF AN OPEN-HEARTH FURNACE

Credit	Per cent	Debit	Per cent
Sensible heat of the gas	14 10	Radiation losses.. ...	40.00
Chemically combined heat of the gas	61.30	Waste gas losses .	30.00
Heat of the pig iron. ...	8 50	Heat content of the steel	15.00
Heat of the air for combustion	0.02	Heat content of the slag	6.00
Heat content of ore, limestone, scrap.	0.01	Heat consumption for the reduction of Fe........	8.90
Combustion of Si in the bath.	0 60		
Combustion of P in the bath.	4.00	Heat consumption for the reduction of Mn.........	0.07
Combustion of C in the bath	10.00		
Combustion of Mn in the bath	0 87	Heat requisite for the reduction of P.	0.01
Combustion of Fe in the bath	0.50		
Combustion of S in the bath..	0.10	Heat requisite for the reduction of S................	0.02
Total	100.00	Total.	100.00

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[1] From HERMANNS. H., "The Planning, Erection, and Operation of Modern Open-hearth Steel Works," Ernest Benn, Ltd., London, 1924.

A complete and carefully worked heat balance of an open-hearth furnace has been published by W. M. Henry and T. J. McLoughlin.[1] This paper contains also a materials balance sheet and the calculation of efficiencies of various parts of the system. A summary of the heat balance is shown in the following tabulation:

Heat received	Per cent	Heat distributed	Per cent
Calorific and sensible heat in fuel	72.6	Absorbed by steel	20.2
Sensible heat in air for combustion	16.6	Absorbed in chemical reactions	2.6
Heat added by chemical reactions	10.6	Latent heat of vaporization in combustion	6.3
Heat in infiltrated air	0.2	Absorbed by cooling water	3.6
		Radiated from bath and port ends	15.0
		Radiated from checkers	2.8
		Radiated from flues	2.0
		Absorbed by air in checkers	16.4
		Lost in waste gases in stack	31.1
Total	100.0	Total	100.0

The following problems deal with heat balances in the metallurgy of iron and steel. Heat balances for various nonferrous metallurgical furnaces are included in later chapters.

Problems

188. In the furnace of Prob 119, the blast is preheated to 650°C. The gases leave the top of the furnace at a temperature of 250°C.

The furnace uses, per ton of pig iron, 500 gal of cooling water, which enters at 10°C and leaves at 60°C.

The slag and pig iron leave the furnace at 1500°C Specific heat of slag, 0 27. Specific heat of pig iron, 0 15

The heat of formation of the slag is 360 Cal. per kilogram of SiO_2. Neglect heat of solution of Mn, Si, and P in the pig iron.

Required: A heat balance of the furnace.

189. An iron blast furnace is assumed to be reducing pure Fe_2O_3 to Fe, and all the reduction is assumed to be performed by CO. For each 960 kg. of Fe produced there is charged 300 kg. of $CaCO_3$, and 800 kg. of pure carbon is burned at the tuyères. The temperature of the blast is 800°C., and that of the escaping blast-furnace gas 200° The slag is 45 per cent CaO. The temperature of the slag and of the iron leaving the furnace is 1600°C. The melting point of the slag and of the iron is 1500°C.

Required: 1. The volume and percentage composition of the blast-furnace gas, per metric ton of Fe produced.

2. The volume of blast required, per ton of Fe.

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[1] "A Thermal Study of an Open-hearth Furnace," *Year Book Am. Iron Steel Inst.*, 1931, pp. 123–162.

3. The percentage of the total calorific power of the fuel which is developed in the urnace.

4. A heat balance of the furnace, per 1,000 kg. of iron reduced.

190. In the blast furnace of Prob. 125 the gases leave the top of the furnace at 350°C., while the blast is preheated to 700°C. The slag flowing out when tapped carries 500 Cal. per kilogram and the pig iron 315 Cal. per kilogram. The heat lost by cooling water used around the tuyères and boshes amounts to 200 Cal. per kilogram of pig iron made. The heat of formation of the slag is 280 Cal. per kilogram of slag.

Required: A heat balance of the furnace, per 1,000 kg. of ore smelted.

191. A magnetite ore is smelted in an electric pig-iron furnace. The ore analyzes as follows:

	Per Cent		Per Cent
Fe_3O_4	78	MgO	5.4
SiO_2	7	S	0.6
Al_2O_3	2	CO_2	2
CaO	3	H_2O	2

Charcoal (assume pure carbon) containing 6 per cent H_2O is used as a reducing agent and amounts to one-fourth of the weight of Fe reduced. Pure SiO_2 is used as a flux to make a slag carrying 33 per cent SiO_2. The pig iron made carries 4 per cent C, 3.5 Si, balance Fe. The slag and pig iron at tapping contain 570 and 330 Cal. per kilogram, respectively.

Assume that all the iron is reduced to Fe and that all the sulphur goes into the slag as CaS. The heat of combination between oxides to form the slag is 150 Cal. per kilogram of $SiO_2 + Al_2O_3$. One-third of the heat supplied in the furnace is from oxidation of carbon and formation of the slag and two-thirds from the electric current. Neglect the oxidation of electrodes.

The gases leave the furnace at 300°C.

Required: 1. The weight of ore, flux, and charcoal needed, per metric ton of pig iron made

2. The percentage composition of the gas leaving the furnace, neglecting any infiltration of air.

3. The kilowatt-hours of electricity required, per ton of pig iron made

4. The percentage of the total heat in the furnace that is represented by the heat content of the pig iron, slag, and gas and by the calorific power of the gas

192. A blast furnace running with 1,154 cu. m. of blast per minute (dry, at 0° and 760 mm.) produces 550 metric tons of pig iron (containing C, 3.5 per cent, Si, 1.5; Mn, 1.0) and 275 metric tons of slag (carrying 3.5 per cent CaS) per day.

Assume the charges (ore, CaO, and coke) to enter the fusion zone at 1350°C. and the gases to leave this zone at 1800°C. The gases here amount to 3,730 cu. m. per ton of pig iron and contain 36 per cent CO, 64 N_2. Assume the weight of SiO_2 and CaO each equal to 50 per cent of the slag.

Assume that the heat of formation of the slag is 100 Cal. per kilogram of slag; of the pig iron, −30 Cal. per kilogram of pig iron.

Heat of fusion of the slag = 120 Cal.
Heat of fusion of the pig iron = 60 Cal.
Specific heat of the liquid slag = 0.25
Specific heat of the liquid pig iron = 0.20
Temperature of the outflowing slag = 1650°C.
Temperature of the outflowing pig iron = 1600°C.
Heat in cooling water = 100 Cal. per kilogram of pig.
Heat conducted to ground = 100 Cal per kilogram of pig
Heat lost by convection and radiation = 50 Cal. per kilogram of pig.

The blast is preheated to 700°C. Assume 10 per cent Fe reduced from FeO in the smelting zone.

Required: 1. A heat balance of the smelting zone, per ton of pig iron.

2. The maximum theoretical temperature of the gases in the hottest part of the smelting zone.

3. The increase of smelting power (percentage) if the blast could be heated to 1000°C., assuming the critical temperature to be 1550°C.

4. The decrease of smelting power if the outside air were saturated with H_2O at 35°C.

5. The increase of smelting power if the blast contained 25 per cent O_2.

193. An acid-lined Bessemer converter blows 30 metric tons of pig iron to pure metal in 24 min. It makes 2,300 kg. of slag, including 100 kg. of SiO_2 corroded from the lining. The slag analyzes SiO_2, 38 per cent; MnO, 12; FeO, 50. The gases consist of 750 cu. m. of CO_2 and 1,500 cu. m. of CO, with the balance N_2. The iron is oxidized at a uniform rate.

The blast pressure is 1,200 mm. gage. The blast enters at 100°C. and the gases escape at 1600°C. The temperature of the pig iron when charged is 1300°C. At the end of the blow the temperature of the slag and metal in the converter is 1650°C.

Required: 1. The volume of air used (standard conditions).

2. The time of each period.

3. The percentage composition of the pig iron.

4. The power required for the blowing engine, at 80 per cent efficiency.

5. A heat balance of the converter. (Assume heat of formation of the slag = 320 Cal. per kilogram of SiO_2.)

194. A basic-lined Bessemer converter contains 20,000 kg. of pig iron containing C, 4 per cent, Si, 1.0; Mn, 1.0, P, 2.2, Fe, 91.8. It is blown down to pure Fe, losing 5 per cent Fe during the blow, this Fe being oxidized at a uniform rate throughout the blow. Assume three distinct periods; in the boil the carbon burns one-third to CO_2 and two-thirds to CO.

The slag must contain not over 12 per cent SiO_2 and CaO is added to dilute it to this percentage.

Air is blown at the rate of 400 cu. m. per minute. The gases escape from the converter at an average temperature of 1500°C. The blast is cold. The lime is preheated to 800°C.

Heat in 1 kg. of pig iron put in = 255 Cal.
Heat in 1 kg. of blown bath = 375
Heat in 1 kg. of slag = 450
Heat of formation slag, per kilogram = 200.

Required: 1. The length of each period of the blow.

2. The weight of lime to be added.

3. The heat generated in the converter by oxidation of the bath and formation of slag.

4. The heat carried out of the converter by the hot gases.

5. A heat balance of the converter.

195. The following pig iron is blown in an acid Bessemer converter, 20 metric tons being charged:

	Per Cent
C	4.0
Mn	0.5
Si	1.4
Fe	94.1

The blow oxidizes all the impurities and 2 per cent of the iron. Assume that oxidation of iron occurs uniformly throughout the blow. Three-fourths of the carbon goes to CO and one-fourth to CO_2.

The air enters at 40°C., and the gases leave at an average of 1420°C. in the first period and 1530° in the second period. Air is supplied at the rate of 550 cu. m. per minute.

The pig iron is at 1250° when charged, and the bath (including the slag) is at 1600° at the end of the blow.

Required: 1. The total volume of air used.

2. The time of each period of the blow.

3. The percentage composition of the gases in each period.

4. The percentage composition of the slag.

5. A heat balance of the operation.

6. The approximate rate of change of temperature of the bath in each period, assuming that one-half the total heat absorbed by the converter is absorbed in each period and that the heat capacity of the bath is the same as for molten iron.

196. An open-hearth furnace treats a charge of 40 tons of molten pig iron and 44 tons of scrap; 5,600 kg. of ore is used for oxidation and 8,000 kg. of $CaCO_3$ as flux.

Pig iron, per cent	Scrap, per cent	Ore, per cent
C 3.6	C 0.5	Fe_2O_3 73
Si 0.9	Si 0.1	SiO_2 15
Mn 1.9	Mn 0.3	MnO 12
P 0.15	P 0 5	

The bath just before tapping carries 0 5 per cent carbon and residual manganese equal to 25 per cent of the original manganese in the pig and scrap, but no silicon or phosphorus.

The slag carries 20 per cent FeO, all of which is assumed to come from oxidation of Fe in the scrap.

The furnace uses as fuel 10,000 kg of oil carrying 82 per cent C, 15 H, 3 N; and 10 per cent excess air is supplied to burn it An additional 50 per cent of excess air leaks in through the furnace doors. There is no CO in the gases.

Following are the temperature data for the furnace.

Incoming materials:

Pig iron	1250°C.
Scrap, ore, limestone, and oil	0°
Air for combustion	1000°
Leakage air	50°

Products:

Steel and slag	1500°C.
Gases	1600°

Heat in pig iron melted at 1200° = 245 Cal., specific heat liquid = 0.15.
Heat in steel melted at 1350° = 300 Cal., specific heat liquid = 0.165.
Heat in slag melted at 1400° = 400 Cal., specific heat liquid = 0.30.
Assume heat of formation of slag = 128 Cal. per kilogram of slag.

Required: 1. A complete charge balance of the furnace.

2. The percentage composition of the steel, slag, and gases.

3. The percentage of the total oxidation performed by the ore.
4. A heat balance of the operation.
5. The thermal efficiency of the regenerators and of the furnace as a whole.

197. A 10-ton electric steel furnace, after being tapped, is charged with 8,000 kg. of steel scrap and 2,000 kg. of pig iron, and during the heat there are charged 100 kg. of ferromanganese, 50 kg. of ferrosilicon, 1,000 kg. of iron ore, and 100 kg. of lime The compositions of the materials charged and the steel tapped are as follows:

	Steel scrap, per cent	Pig iron, per cent	Ferromanganese, per cent	Finished steel, per cent	Ferrosilicon, per cent
Fe	99.0	94	13	98.9	48
C	0.5	4	5	0.6	2
Si	0.2	1	2	0.3	50
Mn	0.3	1	80	0.2	

Iron ore, per cent	Lime, per cent	Electrodes, per cent
Fe_2O_3 90	CaO 100	C 95
SiO_2 8		SiO_2 5
Al_2O_3 2		

100 kg. of electrodes is consumed by air leaking through.

Heat in molten slag tapped = 500 Cal. per kilogram

Heat in molten steel tapped = 325 Cal. per kilogram. Weight of steel, 10,000 kg

Heat of slag formation = 150 Cal. per kilogram of slag. Assume that all the carbon oxidized goes to CO.

Power used, 1500 kw. for 5 hr. The gases escape at 1000°C

Required: 1. A charge balance of materials passing through the furnace.

2. A thermal balance of heat developed and distributed.

3. The net thermal efficiency of the furnace.

CHAPTER X

CALCULATION OF CHARGES FOR SMELTING

The method most often employed for extracting metals from their ores is that of smelting, in which the object is to liquefy the ore by fluxing and melting, at the same time bringing about those chemical changes necessary to produce metal (or sometimes matte) from compounds existing in the ore. An essential feature of the process is that the unreduced parts of the charge shall unite to form slag, which is lighter than the metal or matte, so that separation of the two liquids is effected by gravity. It is essential that the slag shall be of such composition as to melt and flow freely at a temperature readily attained in the furnace. This usually requires mixing the ore with a proper amount of flux. Often also it is necessary or desirable to mix two or more ores in a smelting charge, as well as to include the flux and fuel. It may be necessary, too, to adjust certain other properties of the slag as well as its melting or flowing temperatures. It is not within the province of this book to discuss the properties of different slag compositions or what types of slag the furnace manager should aim for under different conditions. It will be assumed here that the manager has determined what compositions he desires for the slag, and the question to be discussed is in what proportions he shall mix the available materials in order to yield a slag of that desired composition.

The amount of fuel to be used will be based largely on thermal considerations, as discussed in the preceding chapter. In a type of furnace in which the fuel is not mixed with the charge and in which the ash cannot fall on the charge, the amount of fuel used has no bearing on the charge make-up. When, however, all or part of the ash from the fuel becomes a part of the molten mixture, this must be allowed for in determining the charge. As between two possible fuels, the amount of ash and also its percentage composition may be the deciding factors in determining which to use. Usually the ash must be fluxed, but the ash of some fuels may act as a flux itself. Here it will be assumed that the choice of fuel has been made and that the amount to be used has been fixed by the heat requirements of the process or by the amount of reduction required, since in many processes the fuel fills the dual role of heat producer and reducing agent.

Usually the calculation of the charge for smelting will resolve itself into calculation for a desired slag composition, and the slag composition will be gaged by a ratio between the principal slag-forming constituents, such as the ratio $SiO_2:CaO:FeO$ or $SiO_2:Al_2O_3:CaO$. Compounds present in minor amounts may be disregarded, or some of them may be counted in with that principal constituent which they chemically resemble; for example, MnO may be counted with FeO, and MgO with CaO. This is discussed more fully below.

As regards the composition of the metal to be produced by the process, it may be necessary to see that the charge does not contain more than a certain allowable amount of some impurity, as phosphorus or sulphur in iron smelting; but this precaution is readily observed and need not affect the method of calculation. In general it may either be assumed that the metal produced will be the pure element, or—as is usually preferable—it may be assumed that the metal will be of some composition which previous experience has shown will be approximated under the conditions of operation. The composition of the metal is often controlled in the main by such factors as the temperature of the furnace or the amount of reducing agent or of air, and the make-up of the charge need not be adjusted for metal composition, so long as the ore mixture is of a suitable grade and purity. There are exceptions to this, and an important one is in smelting for matte. In this case it is necessary to calculate the charge both with reference to the desired matte composition and with reference to a proper slag. This type of calculation is taken up in a later chapter. It does not differ in general principle from the simpler case.

Several different methods of charge calculation are in use. In each the details of procedure will vary with the kind of smelting process. Once the student has become familiar with the principles of the calculation, he will have little difficulty in changing from one method to another or in applying them to different processes. Two methods will be illustrated here, the same conditions and materials available being used for each, in order to bring out more clearly the points of similarity and difference in the methods themselves. The process will be smelting in the iron blast furnace.

It may be remarked that calculation of charges is not a regular or routine part of furnace operation. When the furnace is running regularly, minor adjustments of charge are often made simply on observation. For example, if it is found that the slag is becoming a little too basic, the furnaceman simply increases a little the proportion of a siliceous ore or reduces the proportion of a basic flux. If it becomes necessary to change to a new ore, which contains, say more silica than one previously used, the flux may simply be increased by an estimated amount. In starting a new furnace it may be possible to make up the charge by simply making it similar to one previously used. In some such cases, however, better results might be obtained by calculation than by this practical trial-and-error method.

In starting to smelt an entirely new ore mixture, a calculation may be indispensable. The charge calculation may be very useful in studying the operation of any furnace with improvement of the operation in view. Often failure to make good use of calculations has been due to inability on the part of the furnace manager, and the ability to handle this type of work may prove a valuable asset to the young engineer.[1]

Calculation of Charge for the Iron Blast Furnace.—Suppose that materials of the following percentage compositions are on hand for smelting:

	Ore *A*	Ore *B*	Ore *C*	Limestone	Coke
Fe_2O_3	68.4	71.4	91.8	1.0	1.7
MnO_2	1.3	4.1			
SiO_2	11.0	14.2	5.3	5.5	5.6
CaO	3.9	2.1	0.2	47.0	0.6
MgO	3.5	1.5	0.1	3.6	0.6
Al_2O_3	6.3	1.7	1.9	1.5	3.8
H_2O	5.6	5.0	0.7	0.5	1.5
CO_2				40.9	
C					86.2

Assume that the composition of the pig iron will approximate the following:

	Per Cent
C	4.0
Si	1.5
Mn	0.5
Fe	94.0

(The assumption as to the pig iron will be based on previous experience. Another type of assumption regarding the Si and Mn might be that certain percentages of all the silica and manganese oxide charged would be reduced, the balance being slagged. For example, it might be assumed that one-half of all the MnO and nine-tenths of all the SiO_2 represented in each material would enter the slag.)

Before beginning the first method of charge calculation with the above materials, it will be desirable to illustrate some of the principles involved with simplified data. The slag of an iron blast furnace is essentially a silicate of lime; the main feature of the fluxing is to add sufficient limestone to supply CaO to flux the SiO_2 in the ore. Assume that the furnace manager in this case has decided to make a slag containing 50 CaO:30 SiO_2, letting the other constituents fall as they may. Assume also that ore *A* is the only ore to be used.

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[1] The subject of charge calculations, though with particular reference to smelting in the lead blast furnace, has been well discussed and illustrated by Boyd Dudley, Jr., *Met. Chem. Eng.*, **16,** 87–98 and 129–34 (1917). Prof. Dudley begins by saying: "Perhaps there is no better way for the student of metallurgy to become familiar with the chemical and metallurgical principles involved in a smelting process than for him to learn something of the calculation of furnace charges to be employed in conducting the operation in question."

Required: 1. The pounds of ore and of limestone to be charged per 1,000 lb. of pig iron produced, disregarding the coke.

2. The same, assuming 1,000 lb. of coke to be used per 1,000 lb. of pig iron.

Solution: Ore *A* contains $^{112}/_{160}$ (or 0.7) × 68.4 = 48 per cent Fe. 1,000 lb. of pig will contain 940 Fe and require $\frac{940}{0.48}$ = 1,960 lb. of ore.

The ore will contain 0.11 × 1,960 = 216 lb. of SiO_2. This will require $^{50}/_{30}$ × 216 = 360 lb. of CaO (neglecting SiO_2 reduced to Si). The limestone carries 47.0 per cent CaO. Therefore, $\frac{360}{0.47}$ = 770 lb of limestone is needed, with 1,960 lb. of ore (1).

The coke will add 56 lb. of SiO_2, requiring, in addition, $^{50}/_{30}$ × 56 = 93 lb. of CaO, or $\frac{93}{0.47}$ = 200 lb. of limestone, making 970 lb. in all (2).

This is the simplest form of solution but is only a rough approximation since it has neglected all but the principal components. Evidently the coke is such a large factor that it cannot be omitted even from the roughest approximation.

Let it now be assumed that a somewhat closer estimate is desired and that two obvious corrections will be made. First, the Si in the pig iron will be taken into account, and, second, the ore itself already contains some CaO and the limestone contains some SiO_2.

The pig contains 15 Si, which came from $^{60}/_{28}$ × 15 = 32 SiO_2. Total SiO_2 to be fluxed = 216 + 56 − 32 = 240 lb.

Total CaO required = $^{50}/_{30}$ × 240 = 400 lb. But the ore contains 0.039 × 1,960 = 76 CaO, and the coke contains 0.006 × 1,000 = 6, a total of 82 lb The net amount to be supplied is therefore 400 − 82 = 318 lb.

The limestone contains 47 0 per cent CaO; but it also contains 5 5 per cent SiO_2, and it must flux its own SiO_2 with some of its CaO, only the remaining CaO being "available" for fluxing the ore.

5 5 per cent SiO_2 requires $^{50}/_{30}$ × 5 5 = 9.2 per cent CaO CaO available = 47 0 − 9.2 = 37.8 per cent

The limestone required therefore = $\frac{318}{0.378}$ = 840 lb., with 1,960 lb. of ore.

Summated Lime.—The next refinement to be made in the calculation is to note that both the ore and the limestone contain other bases, chiefly MgO, besides the CaO, and that these will reinforce the action of the CaO and practically take the place of some of it. Accordingly, there is introduced the principle of "summating" the MgO and sometimes other bases with the CaO. The term "summated lime," written ΣCaO, then includes the lime and other bases. Summation is sometimes done by simple addition of the percentages present, but this practice should not be generally followed. The molecular weight of MgO is 40, while that of CaO is 56. In forming silicates, as $MgSiO_3$ and $CaSiO_3$, 40 parts of MgO will flux the same weight of SiO_2 as 56 parts of CaO. Accordingly, the 3.6 per cent MgO in the ore will do the work of, or is equivalent to, $\frac{56}{40} \times 3.6 = 5.0$ per cent CaO. ΣCaO in the limestone then $= 47.0 + 5.0 = 52.0$ per cent.

Shall the Al_2O_3 also be summated with CaO, or shall it be summated with SiO_2, or with neither? This question has caused much discussion. Whether Al_2O_3 acts as an acid or a base in a slag depends on the composition of the slag. The question will not be discussed here except to say that in general Al_2O_3 reinforces the bases in an acid slag and the acids in a basic slag. In smelting most metals the percentage of Al_2O_3 in the slag is relatively small, and it may be disregarded in the slag calculation. In iron smelting the Al_2O_3 is usually too important to be disregarded. Some managers may decide from their slag type whether the Al_2O_3 should be summated with the SiO_2 or with the CaO and will act accordingly. Probably the best way, however, is to handle Al_2O_3 as a separate constituent in the slag ratio, as, for example, making the desired ratio $CaO:SiO_2:Al_2O_3 = 50:30:15$ and adjusting the charge to yield this slag.

MnO and sometimes an estimated amount of FeO may also be summated with CaO.

As an example of summation, we shall go back to the previous figures and make the ratio $\Sigma CaO:SiO_2 = 50:30$, summating MgO and MnO with CaO but omitting Al_2O_3. FeO will also be omitted; but it will be assumed that the iron of the limestone is not reduced, while the iron of the coke is reduced.

Solution: As above, Fe in ore *A* = 48 per cent and Fe in pig = 940 lb. Fe from coke $= 0.7 \times 17 = 12$ lb. Fe from ore $= 940 - 12 = 928$ lb.

$$\text{Ore required} = \frac{928}{0.48} = 1{,}930 \text{ lb}$$

SiO_2 in ore $= 0.11 \times 1{,}930 = 212$. Adding 56 from the coke and subtracting 32 because of SiO_2 reduced make 236 lb. of SiO_2 to be fluxed. $\frac{50}{30} \times 236 = 393$ lb. of ΣCaO required.

ΣCaO in ore: MnO in ore $= \frac{71}{87} \times 1.3 = 1.06$ per cent. $0.0106 \times 1{,}930 = 20.5$ lb. of MnO. Mn in pig $= 5$ lb. $= \frac{71}{55} \times 5$, or 6.5 lb. of MnO. MnO in slag $= 20.5 - 6.5 = 14$ lb. This is equivalent to $\frac{56}{71} \times 14 = 11$ CaO.

MgO $= 0.035 \times 1{,}930 = 68$ lb., equivalent to $\frac{56}{40} \times 68 = 95$ CaO.

CaO in ore $= 0.039 \times 1{,}930 = 75$ lb. $\Sigma CaO = 75 + 95 + 11 = 181$ lb.

ΣCaO from coke $= 6 + \frac{56}{40} \times 6 = 14$ lb.

ΣCaO needed from flux $= 393 - 181 - 14 = 198$ lb.

As shown above, ΣCaO in the limestone = 52.0 per cent; but 9.2 per cent CaO is needed to flux the SiO_2 in the limestone, leaving 42.8 per cent ΣCaO available. Then $\frac{198}{0.428} = 463$ lb. of limestone needed with 1,930 lb. of ore.

It is obvious from the above calculations that the presence of any considerable amount of MgO greatly reduces the amount of actual CaO needed. When a suitable slag ratio is stipulated, a somewhat larger ratio may be expected for $\Sigma CaO:SiO_2$ than for actual $CaO:SiO_2$. Obviously, the ratio stated in terms of ΣCaO affords a better control.

The calculation of a charge containing ores *B* and *C* as well as *A*, with adjustment for Al_2O_3 as well as SiO_2 and ΣCaO, will now be taken up. Certain preliminary considerations regarding the disposition of ores *A*, *B*, and *C* must be made. It is evident that the principal differences between *A* and *B* are the higher manganese and the lower alumina in *B*. Use of *B* should result in a higher manganese content in the pig iron. Use of *B* alone might result in an undesirably low Al_2O_3 content in the slag, and *A* alone might give too much Al_2O_3 in the slag. The Al_2O_3 then may be adjusted to a suitable proportion by proper mixing of *A* and *B*.

Ore *C* is evidently a very rich ore; and we shall assume, as would usually be the case, that only a limited amount of it is available. There is nothing peculiar about its gangue. The usual practice in such a case is to put a certain fixed amount of this material on each charge, an amount small in proportion to the amounts of the principal ores. In many plants a fixed amount of iron scrap would be used on each charge; ore *C* will be handled in the same manner. Let it be assumed that the manager has decided to use 1 part of *C* for every 5 parts of *A*.

Charge Calculation—Method of Available Flux

Example 21

From the materials listed above, calculate a charge to yield 1,000 lb. of pig iron and a slag having the ratio $SiO_2:Al_2O_3:\Sigma CaO = 32:12:56$. Assume that the pig iron will contain 4 per cent C, 1.5 Si, 1.5 Mn, 93 Fe. The amount of coke used is 960 lb. per 1,000 lb. of pig iron. Assume that 1 part of ore *C* is used to 5 parts of ore *A*.

Solution. The available-flux method begins with taking 100 lb. of the principal ore and calculating the amount of the second ore to be used with this to yield the desired ratio between the SiO_2 and Al_2O_3. The proper amount of coke is then added, and the amount of flux necessary for the proper $SiO_2:\Sigma CaO$ ratio is found.

Take 100 lb. of ore *A*. With this goes 20 lb. of ore *C*. These contain $11.0 + 0.053 \times 20 = 12\ 1$ lb. of SiO_2, which requires $^{12}\!/_{32} \times 12.1 = 4.5$ lb. of Al_2O_3. There is present, in *A* and *C*, $6.3 + 0.019 \times 20 = 6.7$ lb. of Al_2O_3, an excess of $6.7 - 4.5 = 2.2$ lb. To balance this requires $^{32}\!/_{12} \times 2.2 = 5.9$ lb. of SiO_2, to be obtained from ore *B*.

Ore *B* contains 14.2 per cent SiO_2, but its 1.7 per cent Al_2O_3 needs $^{32}\!/_{12} \times 1\ 7 = 4\ 5$ per cent SiO_2. Available SiO_2 in $B = 14.2 - 4.5 = 9.7$ per cent. Weight of *B* to be taken then $= \frac{5.9}{0.097} = 61$ lb.

Fe in $100\ A + 61\ B + 20\ C = 0.7(68.4 + 0.714 \times 61 + 0.918 \times 20) = 91.3$ lb. This will make $\frac{91.3}{0.93} = 98.2$ lb. of pig iron. The coke required for this is $0.96 \times 98.2 = 94.2$ lb.

Total SiO_2 now $= 11.0 + 0.142 \times 61 + 0.053 \times 20 + 0.056 \times 94.2 = 26.0$ lb. But Si in pig iron $= 0.015 \times 98.2 = 1.5$ lb. $= 3.2$ lb. of SiO_2. SiO_2 to be fluxed $= 26.0 - 3.2 = 22.8$ lb. This requires $^{56}/_{32} \times 22.8 = 39.9$ lb. of ΣCaO.

ΣCaO present: MnO_2 in A and $B = 1.3 + 0.041 \times 61 = 3.8$ lb. $= 3.1$ MnO. Mn in pig $= 0.015 \times 98.2 = 1.5$ lb. $= 1.9$ MnO. MnO to slag $= 3.1 - 1.9 = 1.2$ lb. This is equivalent to $^{56}/_{71} \times 1.2 = 0.9$ lb. of ΣCaO.

$MgO = 3.5 + 0.015 \times 61 + 0.001 \times 20 + 0.006 \times 94.2 = 5.0$ lb. $^{56}/_{40} \times 5.0 = 7.0$ lb. of ΣCaO.

$CaO = 3.9 + 0.021 \times 61 + 0.002 \times 20 + 0.006 \times 94.2 = 5.8$ lb.

Total $\Sigma CaO = 0.9 + 7.0 + 5.8 = 13.7$ lb. There is therefore a deficit of $39.9 - 13.7 = 26.2$ lb., to be obtained from the limestone.

ΣCaO in limestone $= 47.0 + {}^{56}/_{40} \times 3.6 = 52.0$ per cent. But the 5.5 per cent SiO_2 requires $^{56}/_{32} \times 5.5 = 9.6$ per cent ΣCaO. Therefore, the available ΣCaO is $52.0 - 9.6 = 42.4$ per cent. Weight of limestone needed $= \frac{26.2}{0.424} = 61.8$ lb.

The charge is now completely balanced with respect to SiO_2 and ΣCaO, the 1.0 per cent Fe_2O_3 in the limestone being negligible. But the limestone and the coke have introduced additional Al_2O_3, which has probably upset the previously obtained balance of SiO_2 to Al_2O_3 and may need additional A or B to take care of it. The Al_2O_3 added is $0.015 \times 61.8 + 0.038 \times 94.2 = 4.5$ lb., which requires $^{32}/_{12} \times 4.5 = 12.0$ lb. of SiO_2. SiO_2 present in the limestone and coke $= 0.055 \times 61.8 + 0.056 \times 94.2 = 8.7$ lb.

As in determining the weight of flux, the SiO_2 reduced to Si must now be deducted from the SiO_2 present. $8.7 - 3.2 = 5.5$ lb. of SiO_2 remaining. There is therefore a deficit of $12.0 - 5.5 = 6.5$ lb. of SiO_2, which can be obtained by using additional ore B; $\frac{6.5}{0.097} = 67.0$ lb. of B is needed. Now this additional B will require additional coke and limestone.

Additional coke $= \frac{0.7 \times 0.714 \times 67.0}{0.93} \times 0.96 = 34.5$ lb.

Additional limestone: SiO_2 in $B = 0.142 \times 67.0 = 9.5$ lb. SiO_2 in extra coke $= (0.056 \times 34.5) - \left(\frac{34.5}{0.96} \times 0.015 \times \frac{60}{28}\right) = 0.8$ lb. ΣCaO needed $= {}^{56}/_{32} \times 10.3 = 18.0$ lb. ΣCaO present in $B = (0.021 + {}^{56}/_{40} \times 0.015)67.0 = 2.8$ lb. (neglecting MnO). ΣCaO present in coke $= 0.014 \times 34.5 = 0.5$ lb. ΣCaO deficit $= 18.0 - 3.3 = 14.7$ lb. Limestone needed $= \frac{14.7}{0.424} = 34.7$ lb.

The charge is now again balanced except that the additional 34.5 lb of coke and 34.7 lb. of limestone will again upset the $SiO_2:Al_2O_3$ ratio. Without going through the calculation again, it is evident that an approximate balance can again be secured by taking additional amounts as follows:

Ore B: $\frac{34.5 + 34.7}{94.2 + 61.8} \times 67.0 = 30.0$ lb
Coke: $^{30}/_{67} \times 34.5 = 15.4$
Limestone: $^{30}/_{67} \times 34.7 = 15.5$

Obviously by repeating this calculation a still closer balance could be obtained, but it is reasonably certain that the above is sufficiently close. The entire charge is now:

Ore $A = 100.$
Ore $B = 61 + 67 + 30 = 158.$
Ore $C = 20.$
Limestone $= 61.8 + 34.7 + 15.5 = 112.$
Coke $= 94.2 + 34.5 + 15.4 = 144.$

In order to yield 1,000 pig iron (= 930 Fe), each of the above amounts must be increased in a certain ratio, the same relative proportions being kept.

Fe in above charge = $0.7(68.4 + 0.714 \times 158 + 0.918 \times 20 + 0.017 \times 144) =$ 141 lb. Ratio of increase = $^{930}\!/_{141} = 6.60$.

Final charge:

Ore *A*:	100 × 6.60 =	660 lb.
Ore *B*:	158 × 6.60 =	1,040
Ore *C*:	20 × 6.60 =	130
Limestone:	112 × 6.60 =	740
	Total =	2,570 lb.
Coke:	144 × 6.60 =	950 lb.

Algebraic Method.—The algebraic method begins by assigning values of x, y, z, etc., to the weights of materials to be determined. The number of unknowns used must not exceed the number of independent equations that can be set up for determination of the unknowns. A preliminary inspection should be made to determine the number of equations possible:

The slag ratio $SiO_2:Al_2O_3:\Sigma CaO = 32:12:56$ will provide three equations, but only two independent ones, since the third is a combination of the two others. Two usable equations are:

$$12 \times \text{wt. of } SiO_2 = 32 \times \text{wt. of } Al_2O_3. \qquad (1)$$

and

$$56 \times \text{wt. of } SiO_2 = 32 \times \text{wt. of } \Sigma CaO. \qquad (2)$$

A third equation is derivable from the total weight of Fe charged, which must equal 93.0 per cent of the pig iron = 930 lb.

Of the four weights to be determined, only three need be counted as algebraic unknowns, since the weight of ore *C* is known in terms of ore *A*. The weight of the coke is 960 lb.

Let

x = pounds of ore *A*.
y = pounds of ore *B*.
z = pounds of limestone.

Then:

$0.2x$ = pounds of ore *C*.

$$\text{Total } SiO_2 = 0.11x + 0.142y + \frac{0.053}{5}x + 0.055z + 0.056 \times 960 - \frac{60}{28} \times 15.$$

$$Al_2O_3 = 0.063x + 0.017y + \frac{0.019}{5}x + 0.015z + 0.038 \times 960.$$

From these and relation (1):

$$-0.690x + 1.160y + 0.18z = 907. \qquad (3)$$

Total ΣCaO: MnO = $^{71}\!/_{87}(0.013x + 0.041y) - {}^{71}\!/_{55} \times 0.015 \times 1{,}000 = 0.0106x + 0.0335y - 19$.

CaO equivalent to this = $0.0084x + 0.0264y - 15$.

$$\mathrm{MgO} = 0.035x + 0.015y + \frac{0.001x}{5} + 0.036z + 0.006 \times 960$$
$$= 0.0352x + 0.015y + 0.036z + 6.$$

CaO equivalent to this $= 0.0493x + 0.0210y + 0.0504z + 8.$

$$\mathrm{CaO} = 0.039x + 0.021y + \frac{0.002x}{5} + 0.47z + 0.006 \times 960$$
$$= 0.0394x + 0.021y + 0.47z + 6.$$

Total $\Sigma\mathrm{CaO} = 0.0971x + 0.0684y + 0.5204z - 5.$

From this and relation (2):

$$3.65x + 5.76y - 13.57z = -1{,}375 \tag{4}$$

Total Fe charged $= 0.7(0.684x + 0.714y + 0.2 \times 0.918x + 0.01z + 0.017 \times 960)$
$= 0.607x + 0.500y + 0.007z + 11.$

The total Fe = 930, or

$$0.607x + 0.500y + 0.007z = 919. \tag{5}$$

Solving Eqs. (3), (4), and (5) simultaneously, $x = 640$, $y = 1{,}050$, $z = 720$.

Final charge:

Ore *A* = 640 lb.
Ore *B* = 1,050
Ore *C* = 130
Limestone = 720
Total = 2,540 lb.
Coke = 960 lb.

Notes.—A device often used which may simplify the calculations is to calculate "simplified compositions" of all materials before beginning the other steps of the charge calculations. In the present problem this would consist of (1) changing all percentages of $\mathrm{Fe_2O_3}$ to percentage of Fe; (2) consolidating the percentage of $\mathrm{MnO_2}$, CaO, and MgO into a single percentage figure for $\Sigma\mathrm{CaO}$; (3) averaging the composition of ore *C* with that of *A* in the proper 5:1 ratio; and, if desired, (4) calculating the amount of coke for the Fe in each material and modifying the percentage composition of each by averaging in the components contributed by this amount of coke, as well as deducting the $\mathrm{SiO_2}$ to be reduced to Si.

The algebraic method gives an instructive view of the relations involved but is more tedious to carry out and is more liable to mechanical error than the arithmetical method.

When the number of materials to be charged is greater than the number whose amounts can be determined by the above methods, it is necessary to decide beforehand on a fixed ratio between the amounts of two or more of them, as was done in Example 21 (page 187) in the case of ores *A* and *C*. In this way the number of unknown quantities to be determined can be reduced to a workable number. This simplifying device is often advisable and sometimes necessary, with the arithmetical method as well as with the algebraic method.

The Cut-and-Try Method.—Two methods of charge calculation have now been illustrated. A third method, known generally as the method of "cut and try," is also of importance. Whether this method is better than either of the two others is a matter of opinion and doubtless depends to some extent on the nature of the process. It was recommended by Boyd Dudley, Jr., for calculation of charges in the lead blast furnace and has been fully explained by him.[1] The method begins with the making of a preliminary estimate of the amounts of the different materials to be placed on the charge, simply by an inspection of their compositions, perhaps aided by a knowledge of which material is on hand in the greatest amount and is therefore to form a principal component of the charge. This preliminary estimate may be in part a guess, but a guess guided by comparing the slag composition desired with the compositions of ore and flux available. The greater the experience of the estimator, the closer will be this preliminary estimate to the final result and the less will be the work involved in arriving at the final result.

The next step in the method is to calculate the products, or at least the slag, that will result from a charge of this chosen composition and then to compare the result with the composition aimed for. For example, it may be calculated that the charge will produce a slag having the ratio $SiO_2 \cdot Al_2O_3 : CaO = 32 : 10 \cdot 48$, whereas the desired ratio was $32 : 12 : 56$. Obviously, the preliminary estimate was deficient in Al_2O_3 by one-sixth and in CaO by one-seventh. The preliminary estimate will now be altered in such a way as to supply these deficiencies as nearly as possible, and the result again calculated. This process of making and correcting estimates and then trying the result will be repeated until the correct charge is obtained to yield the desired result.

The calculation of products yielded by a given charge has been covered at length in Chap. VI. The explanation above should therefore suffice to make clear the procedure of the cut-and-try method without a detailed example.

The following problems are concerned with calculation of charges for the iron blast furnace. Calculation of charges for smelting of copper and lead are included in later chapters, without further discussion of method.

Problems

198. An iron blast furnace smelts an ore mixture having the following composition:

	Per Cent
Fe	58
SiO_2	12
CaO	5

The flux used contains 95 per cent $CaCO_3$ and 5 per cent SiO_2. The coke contains 88 per cent C, 10 SiO_2, 2 CaO.

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[1] Footnote, p. 184.

Required: The weights of ore and flux to be charged to yield 1,000 kg. of pig iron containing 94 per cent Fe, 4 C, 2 Si and a slag having the ratio $SiO_2:CaO = 2:3$, assuming that the furnace requires 950 kg. of coke per ton of pig iron.

199. A blast furnace has, per 1,000 lb. of iron produced, the following slag-forming ingredients to be slagged from the ore and coke:

	Pounds		Pounds
SiO_2	300	MnO	22
Al_2O_3	122	CaO	28
TiO_2	15	MgO	10

The limestone on hand for use as flux analyzes as follows:

	Per Cent
CaO	42
MgO	9
SiO_2	4
Al_2O_3	2
CO_2	43

In this furnace, Al_2O_3 and TiO_2 are counted as acids and are summated with SiO_2.

Required: 1. The weight of flux to be charged to make a slag with the ratio $\Sigma SiO_2:\Sigma CaO = 48:52$.

2. The weight of flux to be charged to make a slag with a silicate degree of 1.8 (*i.e.*, the weight of oxygen in the acid constituents shall be 1.8 times the weight of oxygen in the basic constituents).

3. The percentage composition of the slag in each case

200. The following materials are to be used in a blast furnace:

	Ore *A*, per cent	Ore *B*, per cent	Flux, per cent	Coke, per cent
Fe_2O_3	78	70	4	1
SiO_2	11	16	4	5
Al_2O_3	2	12	2	2
CaO	5	2	46	2
MgO	4		4	
CO_2, C			40	90

1 ton of coke is used per ton of pig iron made.

It is desired to produce a slag having the ratio

$$\Sigma CaO:Al_2O_3:SiO_2 = 55:15:30$$

Assume that the pig iron will contain 95 per cent Fe, 4 C, 1 Si.

Required: Determine the weight of each material (in pounds) to be charged, per 2,000 lb. of pig iron made.

201. An iron blast furnace is charged with materials to yield a slag having the ratio $SiO_2:Al_2O_3:\Sigma CaO = 34:14:52$.

The ores available contain the following (dry analyses):

Ore *A*: Fe_2O_3, 54 per cent; Fe_3O_4, 36; SiO_2, 6; Al_2O_3, 3; CaO 1.
Ore *B*: Fe_2O_3, 79 per cent; MnO_2, 8; SiO_2, 5; Al_2O_3, 6; CaO 2.
Sinter: Fe_2O_3, 84 per cent; SiO_2, 12; Al_2O_3, 4.

The limestone contains CaO 39 per cent, MgO, 13; SiO_2, 3; CO_2, 45. The coke is 88 per cent C, 10 SiO_2, 2 Al_2O_3

The weight of sinter charged is to be three-tenths of the combined weight of ore *A* and ore *B*. The coke is 800 kg. per 1,000 kg of pig iron made.

Assume complete reduction of iron and a pig-iron analysis of 4 per cent C, 1.2 Si, 1.0 Mn, 93.8 Fe.

Required: The weight of each ore, of sinter, and of limestone to be taken, per 1,000 kg. of pig iron made.

202. An iron-blast-furnace plant uses the following materials:

	Ore *A*, per cent	Ore *B*, per cent	Ore *C*, per cent	Limestone, per cent	Coke, per cent
Fe_2O_3	87.0	78.8		1.0	
Fe_3O_4			61.5		
MnO_2	0.4	1.3	0.8		
SiO_2	4.0	5.8	14.7	1.2	9.7
Al_2O_3	2.1	0.9	4.3		0.9
CaO	0.7	0.2	3.6	48.3	1.1
MgO	0.2	0.3	6.8	5.6	
H_2O	5.6	12.7	8.3	0.8	0.6
CO_2				43.1	
C					87.7

It is desired to use 1 lb. of ore *C* for every 2 lb. of ore *B*. The amount of coke required is 0.6 lb. per pound of ore charged. Assume that the furnace reduces to metal 99.5 per cent of the iron oxide, 60 per cent of the MnO_2, and 15 per cent of the SiO_2 charged.

It is desired to make a slag containing SiO_2, Al_2O_3, and ΣCaO in the ratio 20:5:35. Assume that the pig iron contains 4 per cent carbon.

Required: 1. Make up a charge totaling 5,000 lb without the coke to yield the desired slag

2 Calculate the weight and percentage composition of the pig iron and slag produced from this charge.

CHAPTER XI

ALLOYS

The possibility of calculating the properties of a given alloy from a knowledge of its constituents is, in the present state of knowledge, a very limited one. The most useful procedure here, for practical purposes, is experimental measurement of properties and the construction of curves showing the variation with composition. Such curves and tabulations can be found for some alloys in handbooks and special treatises.

It can be stated that a quantitative prediction of the properties of an alloy requires first a knowledge of the form in which the constituents of the alloy exist in relation to each other; *i.e.*, it must be known to which of the standard types the alloy belongs.[1]

If one of the constituents of the alloy is a chemical compound, any calculation based on properties of the elements composing the alloy at once becomes impossible, because the properties of chemical compounds are not directly related to the properties of the elements composing them. In this case it would be necessary to know the properties of the compound.

If the alloy is either a conglomerate (as in eutectic-forming combinations) or a solid solution, the specific volume (the reciprocal of specific gravity) of the alloy may be calculated from the specific volumes of the components by simple weighted averaging, this property being a straight-line function of the composition. If the alloy is a conglomerate, the same statement applies, though less rigidly, to the electrical and thermal conductivities, the hardness, and the tensile strength; *i.e.*, these properties may be approximated by calculation, but the grain structure of the alloy affects them also.

If, on the other hand, the alloy is a solid solution, the same relation does not exist at all with respect to these latter four properties. In this case the conductivity is lowered by the addition of either constituent to the other, the curve falling like a catenary between the two, and the hardness and tensile strength behave in opposite manner, being made greater by adding either constituent to the other and reaching a maximum at the composition having, in a binary alloy, about 50 atomic per cent of each constituent. In cases of this kind, where there is a relation between the properties and compositions but the graph of the relation is curvilinear, a qualitative prediction of properties can be made; but a quantitative one requires exact knowledge of the particular curve, differing with each alloy system.

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[1] It will be assumed here that the student is already conversant with the classification of alloys into types, discussion of which is found in numerous other books. An elementary knowledge of the principles involved in equilibrium diagrams of alloy systems is also assumed.

The calculations to be considered in this chapter will deal principally with determining first the percentages by weight of the metallographic constituents of alloys from the percentages of the elements present, by means of the knowledge imparted by the known constitution diagrams; and, second, the percentages of the field under microscopic examination that would be occupied by these constituents. Calculation of heats of fusion and of specific gravities will also be carried out, these being examples of calculation in which linear variation occurs.

Heat of Fusion of Alloys.—When no chemical compound is formed, the heat of fusion of the alloy is a straight-line function of the composition, except in so far as it may be modified by heat of solution of the components of the alloy in each other. These heats of solution are for the most part unknown quantities. They may be either negative or positive, but perhaps in most cases they are small in comparison with the total heat of fusion and thus may often be neglected. The heats of solution, however, may be of considerable importance if it is desired to know the heat required to make an alloy by melting the constituents together or to set up a heat balance of such an operation. As an example, F. G. Sefing[1] determined calorimetrically the heat of combination between copper and zinc in brass of two-thirds copper, one-third zinc and arrived at the result of 20 Cal. evolved per kilogram of brass. The heat of fusion of this brass is calculated as follows from the heats of fusion of copper and zinc:

$$\begin{aligned} \text{For Cu: } \tfrac{2}{3} \times 57.6 &= 38.4 \\ \text{For Zn: } \tfrac{1}{3} \times 24.4 &= \underline{\ 8.1} \\ \text{Total} &= 46.5 \end{aligned}$$

Since this brass is a solid solution, it would therefore require 46.5 Cal. per kilogram to melt it after heating to the melting point, but to form it from copper and zinc would, on the basis of Sefing's result, require only $46.5 - 20 = 26.5$ Cal., after heating the copper and zinc to their melting points.

Atomic Percentage.—It is sometimes desired to express alloy compositions in percentage according to the relative number of atoms of each constituent present instead of the usual percentage by weight. The "atomic percentages" are readily derived from the weight percentages by dividing the latter by the atomic weights of the respective elements and recalculating the percentages from the relative number of atoms so obtained. For example, the atomic percentages of copper and aluminum in aluminum bronze containing 90 per cent copper and 10 per cent aluminum by weight are calculated as follows:

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[1] "The Heat of Combination of the Constituents of Brass," *Mich. Eng. Expt. Sta.*, *Bull.* 1, 1925.

$$\frac{90}{63.6} = 1.41. \quad \text{Atomic per cent Cu} = \frac{1.41}{1.78} \times 100 = 79.$$

$$\frac{10}{27.0} = \frac{0.37}{1.78}. \quad \text{Atomic per cent Al} = \frac{0.37}{1.78} \times 100 = 21.$$

In this book the commoner practice of stating alloy compositions in percentage by weight will be followed.

Vapor Pressure and Vaporization of Alloys.—This subject is discussed at length in Chap. XXIII.

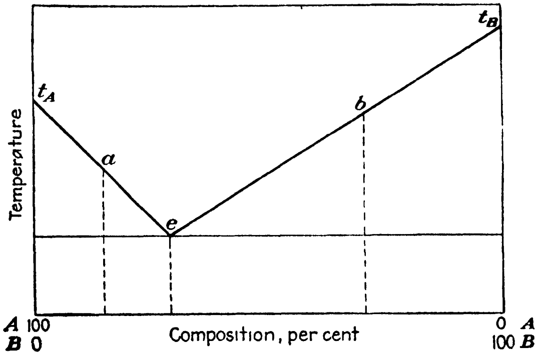

FIG. 5.—Simple eutectic diagram.

Calculation of Metallographic Constitution.—Calculations made from the data of an equilibrium diagram are frequently of importance to the metallurgist, especially in the study of micrographs. The percentages of the different micrographic constituents may be calculated by weight, and from their specific gravities the percentage of the field under a microscope occupied by each may be determined. This calculation may also be employed in the reverse direction, to determine from a micrograph the percentage by weight of the metallographic constituents and hence of the elements of the alloy.

The *eutectic* composition of a series of mixtures of two elements is that composition having the lowest melting point in the series. In a mixture of elements *A* and *B* in the eutectic proportions, 100 per cent of the alloy formed would be eutectic (as at *e*, Fig. 5); but, from a mixture having more of *A* than in the eutectic composition (as *a*, Fig. 5), the resulting alloy would consist partly of crystals of eutectic and partly of separate crystals of the element *A* in excess of the amount of *A* that is bound up with *B* in the eutectic. Likewise, if the mixture contained less of *A* than in the eutectic composition (as at *b*), the resulting alloy would consist of eutectic plus excess *B*.

The amount of "excess" *A* or *B* must freeze or crystallize from a cooling melt before the eutectic crystallizes; it is therefore frequently called *primary* *A* or *B* to distinguish it from the *A* or *B* present in the eutectic. The primary crystals are normally larger than the eutectic-forming crystals and hence are often referred to as the "large" crystals, while those in the eutectic are designated the "small" crystals.

The calculation of the percentages of eutectic and of excess *A* or *B* follows very simply from the percentages of *A* and *B* in the eutectic. For example, given that *A* and *B* form a eutectic containing 40 per cent *A*, let it be required to find the percentage of eutectic and excess *A* in an alloy containing 75 per cent *A* and 25 per cent *B*. Let us for illustration of method arrive at the result in two different ways, diagrammatic and algebraic.

1. *Diagrammatic Method.*—Represent the given compositions on a line as follows:

Per cent *A* 0 40 75 100.

The point 40 will represent an alloy of 100 per cent eutectic, 0 per cent excess *A*. As we go to the right, the percentage of excess *A* increases and that of eutectic correspondingly drops; the point 100 represents 100 per cent *A* and therefore 0 eutectic. The distance from 40 to 100 is 60 units, of which the point 75 represents 75 − 40, or 35 units. Therefore, 75 is $^{35}/_{60}$ of the distance from 40 to 100, and the percentage of excess *A* in the alloy is $^{35}/_{60}$, or 58.3 per cent, leaving 41.7 per cent eutectic.

In an alloy containing less *A* than the 40 per cent in the eutectic, say 30 per cent, the percentage eutectic is obviously $^{30}/_{40}$, or 75 per cent, leaving 25 per cent excess *B*.

The diagrammatic method is sometimes referred to as the "lever" method.

2. *Algebraic Method.*—Let x be the percentage of eutectic in the alloy; then $100 - x$ = per cent excess *A*. The equation follows from the total per cent *A*:

$$0.40x + 100 - x = 75.$$

Solving:

$$-0.60x = -25, \text{ or } x = 41.7.$$
$$100 - x = 58.3.$$

The distinction between primary crystals and eutectic-forming crystals is brought out in Figs. 6 and 7. In Fig. 6 the light areas are large crystals of primary ferrite, which began to form in the cooling steel at about 800°C. The dark areas are pearlite, a eutectoid (see page 201) which formed at about 700°C. The pearlite itself consists of distinct crystals of ferrite and Fe_3C but does not appear to be thus constituted because these crystals are too small to be visible as separate constituents at the magnification of 100 diameters. Figure 7, however, shows pearlite magnified 500 diameters, and the small crystals of ferrite and Fe_3C are both indicated in a somewhat banded arrangement. In this kind of micrograph it is not possible to identify the constituents entirely, as the area appearing dark is probably increased because of shadowing.

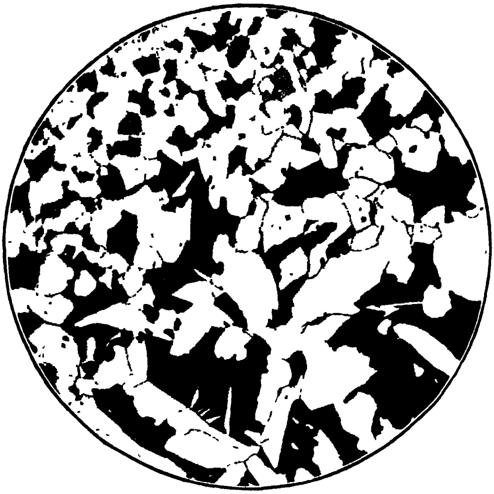

FIG. 6.—Micrograph of structural steel containing 0.30 per cent carbon (× 100).

Calculation of Specific Gravity.—In the above example, suppose the specific gravity of *A* is 2.0 and that of *B* is 7.0. What is the specific gravity of the eutectic?

At first sight it may appear that this question can be answered by a simple summation of specific gravities; since the eutectic is 40 per cent *A* with density 2.0 and 60 per cent *B* with density 7.0, one is tempted to write $0.40 \times 2.0 + 0.60 \times 7.0 = 5.00$. But a closer analysis shows that this summation must be made with the specific volumes, and it is

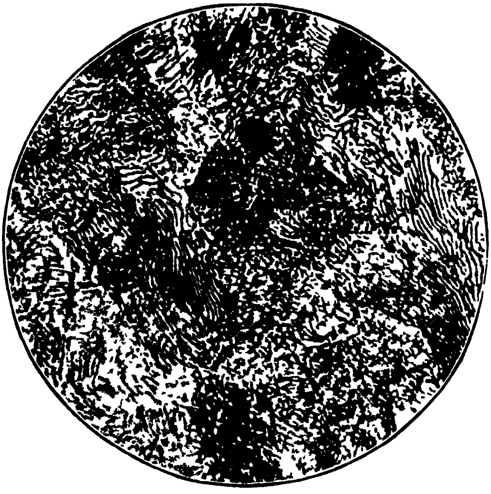

FIG. 7.—Micrograph of pearlite (× 500).

wholly incorrect to add the specific gravities. The correct solution is as follows:

1 g of eutectic contains 0.40 g of *A* and 0.60 g of *B*. 0.40 *A* will occupy $\frac{0.40}{2.0}$ = 0.20 cc., and 0.60 *B* will occupy $\frac{0.60}{7}$ = 0.086 cc., so that 1 g. of eutectic occupies 0.286 cc., and its specific gravity is $\frac{1}{0.286}$ = 3.5.

This shows the possibly curious result that, although the alloy contains a smaller percentage of *A* than of *B*, its specific gravity is nearer that of *A* than of *B*. This is because volumetrically it contains more of the light *A* than of the heavy *B*. Volumes and weights are additive; specific gravities are not.

Calculation of Percentage of Field under the Microscope Occupied by Each Constituent.—The micrograph, or the field seen through the eyepiece of the microscope, is a sectional area. If each crystal seen had its sides perpendicular to the axis of the eyepiece and if every section of the alloy had the same percentage distribution of crystals as the section viewed, then the areas seen would represent absolutely the volumetric composition of the alloy. Obviously this is not the case; yet if several sections were taken it would become approximately so in the average. In most cases the crystal distribution is sufficiently regular that a *single* section will approximately represent the volumetric composition, provided that section is reasonably large, or, in other words, provided the magnification is not too great Hence a micrograph may be used to determine percentage composition by volume and in connection with specific gravities to determine percentage composition by weight, but the method must be used with caution and in most cases is only an approximation at best. If several sections are taken and note is made of the variation from the average, an idea of the precision of the method in any particular case may be gained. The method not only is limited in this way but often is mechanically impossible because of irregularity or fineness of grain structure or indistinctness of grain boundaries. The calculations are nevertheless instructive.

With reference to the previous example, it may be desired to know what percentage of the field is occupied by *A* and by *B*, regardless of whether primary crystals or crystals contained in eutectic. Or it may be desired to know the percentage occupied by eutectic and by primary crystals of *A* or *B*. Let it be required to calculate both these cases with respect to the alloy containing 75 per cent *A*.

In 1 g. of alloy, there are:

$$\frac{0.75}{2.0} = 0.375 \text{ cc. of } A$$

and

$$\frac{0.25}{7} = 0.036 \text{ cc. of } B$$

$$\text{Total} = 0.411 \text{ cc.}$$

Therefore, $\frac{0.375}{0.411} = 91$ per cent of the field is occupied by A and $100 - 91 = 9$ per cent is occupied by B.

The alloy was calculated to be 41.7 per cent eutectic.

In 1 g. of alloy, there are:

$$\frac{0.417}{3.5} = 0.119 \text{ cc. of eutectic}$$

and,

$$\frac{0.583}{2.0} = 0.291 \text{ cc. of excess } A$$

$$\text{Total} = 0.410 \text{ cc.}$$

Therefore, $\frac{0.119}{0.410} = 29$ per cent of the field is occupied by eutectic and $100 - 29 = 71$ per cent by primary crystals of A.

Suppose now a micrograph shows 80 per cent of the field occupied by primary crystals of B and 20 per cent by eutectic. What is the percentage composition of the alloy?

1 cc. of alloy contains:

$$0.80 \times 7.0 = 5.6 \text{ g. of } B,$$

and

$$0.20 \times 3.5 = 0.7 \text{ g. of eutectic.}$$

By weight the alloy is $\frac{5.6}{6.3} = 89$ per cent B, 11 per cent eutectic. The eutectic contains $0.60 \times 11 = 7$ units of B, which, added to the 89 primary B, makes 96 per cent B, 4 per cent A in the alloy.

The micrographic constitution of any alloy containing eutectic may accordingly be calculated on two different bases, one considering the eutectic as a single constituent and the other disregarding the presence of eutectic as a constituent and considering the alloy as resolved into the separate elements. In the problems given at the end of this chapter, calculation on both bases will be required in some cases, but more often the eutectic will be considered a single constituent. Unless stated otherwise, this latter basis should be understood as the desired one, because practically the properties of an alloy are determined by the properties of the eutectic more than by the properties of the separate elements in the eutectic.

Metallographic Calculations for Iron and Steel.—The above examples have employed the simple case of a binary alloy with no compounds or solid solutions. In less simple cases the calculations become more difficult or at least more complex, but the same principles apply. An example will be given, using the iron-carbon diagram, Fig. 8. Since in the cooling of steel and cast iron a change in constitution takes place after the metal has cooled considerably below the freezing point, it is necessary to specify whether the constitution is desired just after freezing or after cooling below the critical range. A complication arises in dealing with cast iron, in that usually part of the carbon is precipitated as graphite; the amount so precipitated must be specified.

As can be seen in Fig. 8, the solid solution (austenite) formed when steel freezes breaks up at lower temperatures into ferrite (Fe) and cementite (Fe_3C). The temperature at which crystals of either of these is formed depends on the percentage of carbon present; and when there is 0.83 per cent carbon, we have the lowest temperature, all the solid solution breaking up at this temperature as in the formation of a eutectic in freezing. A structure formed in the manner of a eutectic but entirely in the solid state is called a *eutectoid*, and the eutectoid of ferrite and cementite is called *pearlite*. (The formation of pearlite alone presupposes normal slow cooling; with rapid cooling, as in quenching, other structures such as martensite or troostite may result; these will not be studied in this book.)

As above, the eutectic of austenite and cementite (sometimes called *ledeburite*) may be regarded in calculations as a single constituent or may be disregarded and only the austenite and cementite accounted for. Likewise, pearlite may be regarded as a constituent, or the steel may be considered as resolved only into ferrite and cementite. In the usual case, pearlite should be considered as a constituent, together with excess ferrite in steels of less than 0.83 per cent carbon and excess cementite in steels of more than 0.83 per cent carbon.

The diagrammatic method illustrated above is recommended for determination of the percentages of the different constituents. As an aid in attacking problems on the constitution of steel and cast iron, the constituents are listed in Table IV, the percentage of carbon in each serving as a reference point in the calculation of percentages by the diagrammatic method. In this table the point 6.68 is obtained from the atomic weights in the compound Fe_3C, thus: $\frac{12}{3 \times 55.84 + 12} = 0.0668.$ The values 1.7, 4.3, and 0.83, however, result from experimental determination. Owing to the experimental difficulties involved, there is considerable uncertainty as to the exact location of these points, and slightly different values have been used by different writers.[1]

With the aid of Table IV, calculation of the constituents of steel and cast iron may be made without consulting the iron-carbon diagram, but it is good practice to refer to the diagram (Fig. 8) as an aid in visualizing the relations involved. In problems on gray cast iron neither of the points 6.68 or 100 can be used alone, since the carbon will be divided between Fe_3C and graphite. When the proportion in which it is divided is known (which in a problem must be given in some way), the calculation follows as illustrated in part 3 of Example 22.

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[1] The values used in Table IV and in Fig. 8 are those recommended by Samuel Epstein, "The Alloys of Iron and Carbon," Vol. I—Constitution, McGraw-Hill Book Company, Inc., New York, 1936.

It should be noted that in all the problems considered here, the presence of elements other than iron and carbon is disregarded. These would alter relations or change the reference points to a greater or less extent, depending on which elements were present and in what amounts; but the amounts of other elements present in plain carbon steel do not cause an important displacement. The presence of silicon in cast iron is an important determinant of the amount of graphite, silicon tending to cause precipitation of carbon as graphite instead of retention as Fe_3C.

TABLE IV.—REFERENCE POINTS IN THE IRON-CARBON DIAGRAM

Constituents just after freezing	Carbon, per cent	Constituents after slow cooling to room temperature	Carbon, per cent
Austenite (saturated)	1 7	Ferrite (Fe)	0
Eutectic	4.3	Pearlite (Fe-Fe_3C)	0 83
Cementite (Fe_3C)	6 68	Cementite (Fe_3C)	6 68
Graphite (C)	100 0	Graphite (C)	100 0

The percentages of ferrite and pearlite contained in the steel shown in Fig. 6 can readily be estimated from the photomicrograph by measurement of the respective areas, which perhaps might best be done by cutting apart the dark and light areas from the photomicrograph and weighing them separately on a balance. Figure 7, however, does not afford a satisfactory specimen for such a determination.

Making a rough visual estimate of the amount of pearlite in Fig. 6, one would place it at a little over a third and certainly less than half; call it two-fifths. The difference in the specific gravities of ferrite and pearlite being small, the percentage of carbon in the steel would be about $\frac{2}{5} \times 0.83 = 0.33$ per cent. Actual measurement would arrive closer to the stated figure of 0.30 per cent. In Fig. 7, since the steel is known to carry 0.83 per cent C, the areas of Fe_3C must occupy about $\frac{0.83}{6.68} =$ about one-eighth of the field, the small difference in specific gravities being neglected.

Notes on the Iron-carbon Diagram (Fig. 8).—The dotted portion of the line *AE* denotes that the small and relatively unimportant area occupied by the delta phase has, for the purposes of this book and for the sake of simplicity, been omitted. The lines *PG* and *PQ* have also been omitted for the same reason, and it is expected that calculations will be made as though *P* were at 0 per cent carbon instead of in its actual position at 0.04 per cent.

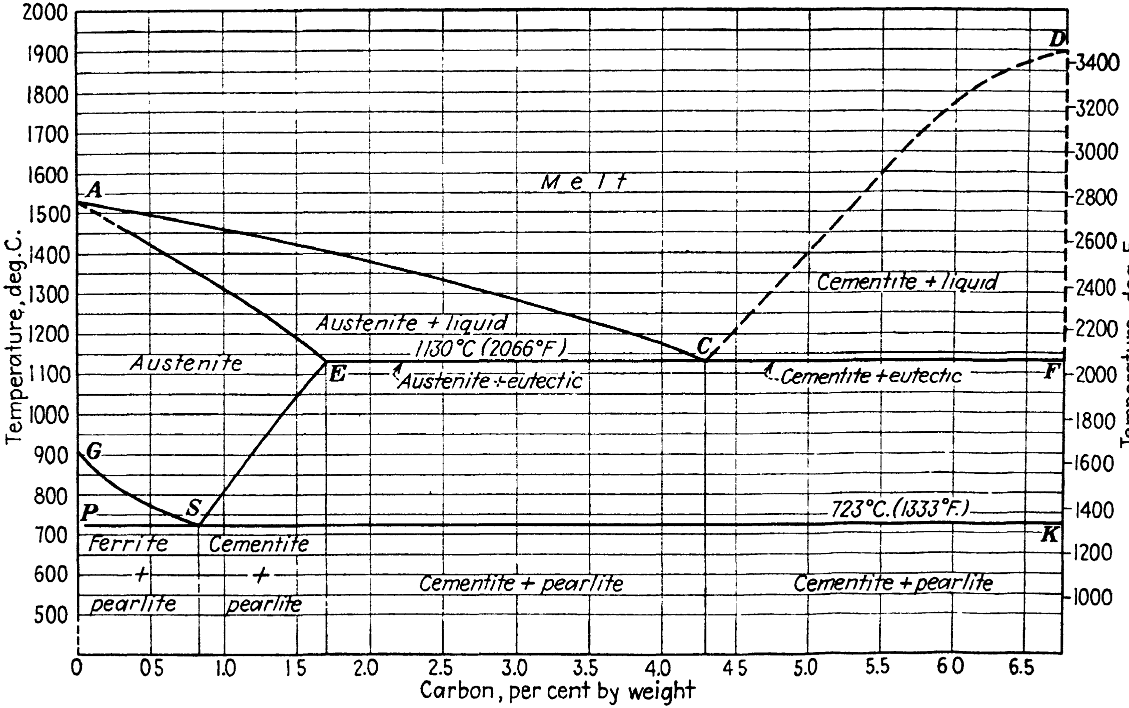

FIG. 8.—Constitution diagram of the system iron-iron carbide (modified). For the purposes of this book the diagram has been modified as stated in the notes, page 202; in other respects it is essentially the diagram given by Samuel Epstein, *op. cit.*, p. 96.

The points in the diagram are those for the system iron-Fe_3C. In the iron-graphite system the positions of some of the points are shifted somewhat, it seems best for the present purpose not to take account of these small differences, but to calculate for graphite with the same diagram as for Fe_3C.

Example 22

1. A steel is composed of 50 per cent pearlite and 50 per cent ferrite. What were its components and percentages just after freezing?

2. If its carbon content were seven times as great, what would be its components and their percentages just after freezing and at room temperature?

3. 4.5 kg. of carbon is dissolved in 95.5 kg. of molten iron. In cooling, the carbon in excess of the eutectic separates as graphite, and two-thirds of the remaining carbon also separates as graphite.

a. What percentages of pearlite, cementite, and graphite would the alloy contain when cold?

b. What percentages of ferrite, cementite, and graphite?

c. In cases *a* and *b*, what percentage of the field under the microscope would be occupied by each constituent?

(Specific gravity: graphite, 2.25; ferrite, 7.86; cementite, 7.66)

4. A photomicrograph of steel shows 30 per cent of the area occupied by pearlite and 70 per cent by ferrite. How much carbon does the steel carry?

5. A photomicrograph of cast iron shows 4 per cent of the area occupied by graphite, 35 by cementite, and 61 by ferrite. Assuming that no graphite had separated immediately after freezing, what percentage of austenite and cementite (by weight) did the alloy then contain?

Solution: The carbon content of the steel is $0.50 \times 0.83 = 0.415$ per cent In Table IV any carbon percentage below 1.7 represents austenite, which is a solid solution of any amount of carbon up to 1 7 per cent In Fig 8 also it is seen that this steel just after freezing was 100 per cent austenite (1)

$7 \times 0.415 = 2.905$ per cent carbon (point x) This point lies between E (1 7) and C (4.3) on the line ECF, Fig. 8. Since E is the austenite point and C the eutectic point, the constituents are austenite and eutectic. The distance EC is $4.3 - 1\ 7 = 2.6$ units, of which Ex covers $2.905 - 1.7 = 1.205$ units. The sample is therefore $\frac{1.205}{2.6} = 46$ per cent eutectic, and $100 - 46 = 54$ per cent austenite (2)

If the eutectic be disregarded as a constituent, the components are austenite and Fe_3C. We then have $\frac{2\ 905 - 1\ 7}{6.68 - 1.7} = 24$ per cent Fe_3C, 76 austenite (2)

At room temperature, the point x lies between S and K on the line PSK The constituents are therefore pearlite and Fe_3C or, if pearlite be not counted, ferrite and Fe_3C. The percentages are:

$$\frac{2.905 - 0.83}{6\ 68 - 0.83} = 35.5 \text{ per cent } Fe_3C, \ 64.5 \text{ per cent pearlite}$$

or

$$\frac{2.905}{6.68} = 43.5 \text{ per cent } Fe_3C, \ 56.5 \text{ per cent ferrite (2).}$$

Carbon in excess of eutectic $= 4.5 - 4.3 = 0\ 20$ per cent.
Total graphite $= 0.20 + \frac{2}{3} \times 4\ 3 = 3.1$ per cent.
Total C in $Fe_3C = 4\ 5 - 3.1 = 1\ 4$ per cent. After deducting the 3.1 per cent graphite, there remains 96.9 per cent of the alloy, and the 1.4 per cent C in Fe_3C will constitute $\frac{1.4}{0.969} = 1.45$ per cent of this remainder.

$\frac{1.45 - 0.83}{6.68 - 0.83}$ = 10.6 per cent cementite, 89.4 per cent pearlite; but these are percentages of the sample without its 3.1 per cent of graphite, or 96.9 per cent of the total sample:

$$0.969 \times 10.6 = 10.3 \text{ per cent cementite.}$$
$$0.969 \times 89.4 = 86.6 \text{ per cent pearlite}$$
$$3.1 \text{ per cent graphite (3}a\text{).}$$

Disregarding pearlite:

$$\frac{1.45}{6.68} = 21.7 \text{ per cent cementite, } 78.3 \text{ per cent ferrite.}$$
$$0.969 \times 21.7 = 21.0 \text{ per cent cementite.}$$
$$0.969 \times 78.3 = 75.9 \text{ per cent ferrite}$$
$$3.1 \text{ per cent graphite (3}b\text{).}$$

The specific gravity of pearlite must be calculated. Pearlite = $\frac{0.83}{6.68}$ = 12.4 per cent Fe_3C, 87.6 per cent ferrite.

$$0.124 \text{ g. of } Fe_3C = \frac{0.124}{7.66} = 0.0162 \text{ cc.}$$
$$0.876 \text{ g. of Fe} = \frac{0.876}{7.86} = 0.1115$$
$$\text{Total} = 0.1277 \text{ cc.}$$
$$\text{Sp. gr.} = \frac{1}{0.1277} = 7.83$$

Case *a*:

$$\text{Cementite} = \frac{10.3}{7.66} = 1.35 \text{ cc.} = 9.5 \text{ per cent of field}$$
$$\text{Pearlite} = \frac{86.6}{7.83} = 11.06 \text{ cc.} = 80.2 \text{ per cent of field}$$
$$\text{Graphite} = \frac{3.1}{2.25} = 1.38 \text{ cc.} = 10.0 \text{ per cent of field (3}c\text{)}$$
$$\text{Total} = 13.79 \text{ cc.}$$

Case *b*:

$$\text{Cementite} = \frac{21.0}{7.66} = 2.74 \text{ cc.} = 19.9 \text{ per cent}$$
$$\text{Ferrite} = \frac{75.9}{7.86} = 9.66 \text{ cc.} = 70.1 \text{ per cent}$$
$$\text{Graphite} = \frac{3.1}{2.25} = 1.38 \text{ cc.} = 10.0 \text{ per cent (3}c\text{)}$$
$$\text{Total} = 13.78 \text{ cc}$$
$$0.30 \times 7.83 = 2.35 \text{ g}$$
$$0.70 \times 7.86 = 5.50$$
$$\text{Total} = 7.85 \text{ g}$$

The steel is therefore $\frac{2.35}{7.85}$ = 29.9 per cent pearlite by weight.

$$0.299 \times 0.83 = 0.25 \text{ per cent carbon (4).}$$
$$0.04 \times 2.25 = 0.09 \text{ g. of graphite} = 1.2 \text{ per cent.}$$
$$0.35 \times 7.66 = 2.68 \text{ g. of cementite} = 35.5 \text{ per cent.}$$
$$0.61 \times 7.86 = 4.79 \text{ g. of ferrite} = 63.4 \text{ per cent.}$$
$$0.355 \times 6.68 = 2.37 \text{ C in cementite}$$
$$1.2 \text{ C in graphite}$$
$$3.57 \text{ C in the alloy}$$

$\frac{3.57 - 1.7}{66.8 - 1.7}$ = 38 per cent cementite, 62 per cent austenite (5).

Problems

Many of the following problems contain requirements that can be answered without calculation by inspection of the constitution diagram. These have been inserted to afford practice in the interpretation of the diagrams. Ability to answer these requirements is assumed without discussion of the principles here.

203. Two metals, *A* and *B*, are used to form a series of alloys. *A* and *B* form a eutectic containing 59 per cent *A* and 41 per cent *B* but do not form any compounds or solid solutions.

The specific gravity of *A* is 9.0; of *B*, 6 0.

Consider three mixtures containing, respectively, 10, 50, and 80 per cent *A*, 90, 50, and 20 per cent *B*.

Required: 1. The percentages of eutectic and excess *A* or *B* (which?) contained in each of these mixtures after freezing.

2. When a section of each mixture is examined under the microscope, what percentage of the field in each case would be occupied by:

a *A* and *B*, regardless of size of crystals or whether contained in the eutectic or not?

b. Eutectic and excess *A* or *B*?

3. If the field was 70 per cent eutectic and 30 per cent excess *A*, what percentages of *A* and *B* did the mixture contain by weight?

204. A series of alloys is made up of the components *X* and *Y*, which do not enter into chemical combination with each other and are mutually insoluble in the solid state. A eutectic is formed containing 19 per cent *X*, 81 per cent *Y*.

The heat of fusion of *X* is 60 cal. per gram, of *Y*, 24 cal. per gram When *X* and *Y* are dissolved in each other after melting, in the proportion of 3*X* to 1*Y*, 13 cal is evolved per gram of alloy formed

The specific gravity of *X* is 8.2; of *Y*, 5.7.

Required 1. The percentages of eutectic and of primary *X* or *Y* (which?) in each of the alloys containing 75, 30, and 10 per cent *X*.

2. The percentages of the field under a microscope occupied by eutectic and by primary crystals in each of these alloys

3. The heat required to melt the constituents together and form 100 g of the molten alloy containing 75 per cent *X*.

205. Pure antimony melts at 630°C. and lead at 327°C When alloyed together these metals form no compounds and only a negligible amount of solid solution but form a eutectic carrying 13 per cent antimony and freezing at 247°C. Assume that the liquidus lines connecting these points are straight lines.

Three melts are made as follows:

A: 50 per cent lead, balance antimony.
B: 87 per cent lead, balance antimony.
C: 96 per cent lead, balance antimony.

Required: 1. The temperature at which lead or antimony (which?) will begin to crystallize from melts *A* and *C*.

2. The temperature at which each melt will be completely solidified.

3. The percentage of eutectic contained in each alloy after freezing.

4. The specific gravity of the eutectic.

5. If polished sections of each alloy were examined under the microscope, what percentages of the field (on the average) would be occupied (*a*) by antimony and by lead; (*b*) by eutectic and crystals of antimony or lead in excess of that in the eutectic?

6. How much heat would be liberated or absorbed (which?) during freezing of 1 kg. of each of these alloys?

206. Gold and nickel form a eutectic containing 25 per cent nickel and 75 per cent gold, melting at 950°C. A small amount of solid solution of undetermined composition is formed; this may here be neglected. No compounds are formed.

Three alloys are made by melting together:

A: 10 parts nickel, 90 parts gold.
B: 25 parts nickel, 75 parts gold
C: 90 parts nickel, 10 parts gold

Required· 1. Construct the gold-nickel equilibrium diagram, assuming the liquidus and solidus lines to be straight.

2. The temperature at which gold or nickel (which?) will first begin to freeze in each of these alloys as it cools from the molten state

3. The temperature at which each alloy will be entirely crystallized.

4. The quantity of heat liberated or absorbed (which?) during the freezing of 1 kg. of each of these alloys. (Neglect heats of solution.)

5. If sections of each of these alloys (slowly cooled) were examined under the microscope, what percentage of the field (on the average) would be occupied by gold and by nickel (not necessarily in large crystals)?

6. What percentage of the field would be occupied by large crystals of gold or nickel (which?), and by eutectic?

207. Pure tin freezes at 232°C. Alloyed with zinc it forms a eutectic containing 8 per cent zinc and freezing at 192°C The alloy of 80 per cent tin with 20 per cent zinc begins to freeze at 270°C., that of 50 per cent tin with 50 per cent zinc at 360°C. No solid solution or chemical compound is formed

Three melts are made as follows·

A. 5 lb of zinc dissolved in 95 lb of tin.
B. 8 lb. of zinc dissolved in 92 lb. of tin
C· 30 lb. of zinc dissolved in 70 lb. of tin

Required: 1 The temperatures at which tin or zinc (which?) would first begin to crystallize from melts *A* and *C*

2. The temperature at which each melt would be completely solidified.

3. The percentages of eutectic and of excess tin or zinc contained in each alloy after freezing

4. What percentage of tin would be contained in the alloy having 40 per cent primary zinc?

5. Calculate the atomic percentage composition of alloys *A* and *C*.

208. Three solders are made by melting lead and tin together. They contain by weight 40 per cent tin, 69 per cent tin, and 80 per cent tin. The solid solubility of lead in tin is nil, and that of tin in lead may here be neglected; no compounds are formed. The melting point of the eutectic is 181°C The eutectic is composed of 63 per cent tin, 37 per cent lead.

Latent heat of fusion of lead, 5.9 Cal. per kilogram
Latent heat of fusion of tin, 14.5 Cal. per kilogram

Required: 1. The temperature at which lead or tin (which?) will first begin to crystallize from each of the alloys as it cools.

2. The amount of heat liberated or absorbed (which?) during the freezing of 1 kg. of each of these alloys. (Neglect heat of solution.)

3. If sections of each of these alloys (slowly cooled) were examined under the microscope, what percentage of the field, on the average, would be occupied by lead and by tin (not necessarily in large crystals)?

4. What percentage of the field would be occupied by large crystals of lead or tin (which?) and by eutectic?

209. Aluminum and silicon form a eutectic containing 11.6 per cent silicon. No compound is formed, and the amount of solid solution is negligible. The freezing point of the eutectic is 577°C.

Required: 1. The percentages of eutectic and of excess aluminum or silicon (which?) in the casting alloys containing 5 per cent silicon and 13 per cent silicon, assuming normal slowly cooled alloys

2. When one of this series of alloys is examined under the microscope, it is found that 60 per cent of the field is occupied by areas of primary aluminum. What percentage of silicon did this alloy contain, by weight?

3. At what temperature did the primary crystals begin to separate from this alloy and also from the alloy of 5 per cent silicon? (Assume that the freezing points in the diagram are connected by straight lines.)

4. What is the atomic percentage of silicon in the 13 per cent alloy?

210. Consider three iron-carbon alloys, as follows: *A*, 0.15 per cent carbon; *B*, 0.83 per cent; *C*, 1.0 per cent.

Required: 1. The constituents and their percentages by weight in each of these alloys just after freezing.

2. The same at room temperature, counting pearlite as a single constituent.

3. The same, disregarding pearlite as a constituent.

4. How much ferrite and cementite will *B* be composed of at room temperature, in percentage of field occupied in a section?

211. Two specimens of steel, *A* and *B*, may be regarded as composed either of ferrite (Fe) and cementite (Fe_3C), or else of Fe_3C and pearlite or ferrite and pearlite, depending on the carbon content.

A: sheet steel containing 0 20 per cent C.
B: spring steel containing 0 95 per cent C.

Required: 1. When *A* and *B* are cooled from the molten state, at what temperatures do they begin to crystallize, and at what temperatures is solidification complete?

2. What will be their metallographic compositions just after freezing and at room temperature, regarded in each of the above ways?

3. If sections of *A* and *B* are examined under the microscope, what percentages of the field will be occupied by ferrite and by Fe_3C?

4. Above what temperatures should *A* and *B* be heated before quenching to obtain the maximum hardening effect?

5. A steel is composed of 40 per cent pearlite and 60 per cent ferrite. How much carbon does it contain? How much Fe_3C?

6. A photomicrograph of steel shows 10 per cent of the area occupied by Fe_3C, and 90 per cent by ferrite. How much carbon does the steel contain? How much pearlite?

212. Three samples of steel contain the following:

A: 0.30 per cent carbon.

B: 88 per cent pearlite and 12 per cent cementite, by weight.

C: two-thirds pearlite and one-third ferrite, by cross-sectional area, as seen under the microscope.

Required: 1. What is the percentage constitution of *A* just after freezing? What is it at room temperature, both with the pearlite as a single constituent and also broken down into its components?

2. Compute the specific gravity of pearlite.

3. What are the percentage constitutions of alloys *B* and *C* at room temperature if the pearlite be considered resolved into its constituents (by weight)?

4. If the carbon content of alloy *A* be tripled, what will be the percentage constitution of the new alloy at room temperature with the pearlite unresolved (*i.e.*, considered as a single constituent)?

213. Consider three alloys as follows:

Pure steel with 0 40 per cent carbon.
Pure steel with 0 83 per cent carbon.
Pure steel with 1 35 per cent carbon

Required: For each of the three alloys, give:

1 The temperature at which the solid solution begins to decompose, naming the constituent or constituents that are precipitated

2 The temperature at which the decomposition of the solid solution is completed.

3. In each alloy, what percentage of the field seen under the microscope will be occupied by·

a. The excess constituent? (Name it)
b. Pearlite?
c Total Fe and total Fe_3C?

4. The field of a photomicrographic section shows 10 per cent excess Fe_3C and 90 per cent pearlite. How much carbon does the steel contain?

5. Assume that the elongation of Fe is 40 per cent

Assume that the elongation of pearlite is 5 per cent.

Assume that the elongation of any intermediate alloy is proportional to the volume of Fe and pearlite which it contains. Compute the elongation of an iron-carbon alloy containing 0 43 per cent carbon.

214. Consider three samples of steel, as follows:

A: 0 20 per cent carbon
B: 80 per cent pearlite and 20 per cent ferrite, by weight.
C: 95 per cent pearlite and 5 per cent cementite, by cross-sectional area.

1. What is the percentage constitution of *A* just after freezing and at room temperature?

2. What are the percentage constitutions of *B* and *C* if the pearlite be considered resolved into its two constituents (both by weight)?

3 What were the percentage constitutions of *B* and *C* just after freezing?

4. If the carbon content of *B* were tripled, what would be the percentage constitution just after freezing:

a. Counting eutectic as a single constituent and all the carbon combined?
b Resolving the eutectic into austenite and cementite, and counting the carbon as one-tenth graphite?

5 Under the conditions of 4*b*, what would be the percentage constitution at room temperature?

215. 1. For the iron-carbon alloys containing 0.83 and 1.5 per cent carbon, give:

a. The temperature at which freezing begins
b. The temperature at which freezing ends.
c. The percentage of each constituent present at 900°C. and at room temperature.

2. In the cooling of a certain iron-carbon alloy from the liquid state, graphite begins to separate out at a temperature of 1400°C. What is the percentage of carbon in the alloy, and what will be the constituents and their percentages when the alloy has cooled to 1000°C.?

216. Five alloys of iron and carbon are made, containing, respectively, 0.3, 1.0, 3.0, 4.3, and 4.5 per cent carbon. These are melted and then slowly cooled to room temperature.

In the first three alloys the carbon is all combined as Fe_3C, but in the last two alloys the carbon that crystallizes during freezing does so as graphite.

Required. 1. The temperature at which each of these alloys will begin to freeze, and the temperature at which solidification will be complete.

2. Give the constituents existing in each of these alloys (*a*) just after freezing, (*b*) at room temperature.

3. Give the percentage by weight of each constituent (*a*) just after freezing, (*b*) at room temperature.

217. Determine the data called for below with regard to the following:

A: mild steel carrying 0.20 per cent carbon.
B: eutectoid steel carrying 0.83 per cent carbon.
C: white cast iron carrying 2.8 per cent carbon, free from graphite.
D: gray cast iron carrying 4.0 per cent carbon, with the carbon assumed to be one-half combined and one-half graphitic after cooling

Required: 1. The temperatures at which the freezing of each of the alloys begins and ends.

2. The constituents existing in each of the alloys, immediately after freezing, and after cooling slowly to room temperature.

3. The percentage of the constituents in each case

218. 1. An iron-carbon alloy contains 1 2 per cent carbon. When slowly cooled, what are its constituents and their percentages just after freezing and at room temperature?

2. The same, for an iron-carbon alloy containing 0.2 per cent carbon.

3. An iron-carbon alloy contains 4.5 per cent carbon What are its constituents and their percentages after slowly cooling to room temperature, assuming that one-third of its carbon separates as graphite?

4. An iron-carbon alloy is composed of 15 per cent ferrite and 85 per cent pearlite What would be its constituents and their percentages if its carbon content were doubled?

5. An iron-carbon alloy is composed of 45 per cent cementite, 54.5 pearlite, 0.5 graphite. If just after freezing it contained only austenite and cementite, what percentage of each did it then contain?

219. For the iron-carbon alloys listed below determine:

1. The temperatures of beginning and completion of freezing when cooled from the molten state.

2. What constituents exist when freezing is just complete?

3. What constituents exist at room temperature?

4. The percentage of each constituent present in each case

5 The percentage of the field under the microscope occupied by each constituent at room temperature

A: structural steel of 0.35 per cent carbon

B: white cast iron of 2.5 per cent carbon, all combined.

C: gray cast iron of 4 3 per cent carbon, assuming that all the carbon is combined just after freezing but that one-half of the carbon is graphitic after cooling.

D: gray cast iron of 4.6 per cent carbon, assuming that the eutectic was entirely graphitic but that the austenite on cooling yields its carbon entirely as combined carbon

220. 1 For the iron-carbon alloys containing 2 5 and 4.3 per cent carbon, give:

a. The temperature at which freezing begins

b The temperature at which freezing ends

c The percentage of each constituent present at 1130°C and at room temperature

Assume that in freezing the carbon separates from the first of these alloys in the form of cementite, from the second, as graphite.

2. A certain iron-carbon alloy at room temperature contains by weight 6 84 per cent cementite and 93 16 per cent pearlite At what temperature would it begin to freeze, and what would be its constituents and their percentages when the alloy has cooled to 1000°C.?

221. 1. An iron-carbon alloy contains 1 45 per cent carbon and 98 55 per cent iron.

What is its metallographic constitution just after freezing?

What is its constitution at room temperature considering (*a*) the pearlite as such; (*b*) the pearlite decomposed?

2 A photomicrograph of steel shows 15 per cent of the area occupied by cementite and 85 per cent by ferrite.

How much carbon does the steel contain?

How much pearlite?

3 An iron-carbon alloy contains 4 7 per cent carbon and 95 3 per cent iron.

What is its percentage constitution just after freezing, assuming 0 3 per cent C as graphite?

What is its percentage constitution at room temperature, assuming one-half of its carbon separating as graphite?

4 An iron-carbon alloy is composed of 20 per cent ferrite and 80 per cent pearlite.

If the carbon content were doubled, what would be its percentage constitution at room temperature (*a*) with pearlite considered as a single constituent, (*b*) with pearlite resolved into its components?

5 An iron-carbon alloy is composed of 45 per cent cementite, 54 1 pearlite, 0 9 graphite, by weight.

If just after freezing it contained only austenite and cementite, what percentage of each would be present?

6 The same as 5, but with the given percentages applying to the percentage of the field occupied under the microscope instead of percentage by weight.

CHAPTER XII

THE MASS LAW AND CHEMICAL EQUILIBRIUM IN METALLURGICAL REACTIONS

When the products of a chemical reaction remain in contact with each other, they may to a certain extent react to form the original reacting substances again. There is strong evidence that this reversal always takes place to some degree, and the net result in a given direction is due to the fact that the reaction proceeds at a greater velocity in one direction than in the other. When conditions are such as to produce equal reaction velocities in both directions, a net conversion of reactants into products no longer continues and *equilibrium* results.

Equilibrium is usually undesirable in metallurgical processes, where it is desired to have a reaction proceed as completely and rapidly as possible. Nevertheless, it frequently constitutes an important problem, and much study has been given to it in recent years. For example, when the impurities are oxidized and carried into the slag in the open-hearth steel process, equilibrium between the reactants in the steel and the products in the slag determines the degree of elimination of the impurities, and quantitative study of this process from the standpoint of equilibrium has been very profitable, even though equilibrium is probably never reached in the furnace.

In this chapter we shall introduce the principles involved in equilibrium calculations and give some examples of their use. The question is too large, however, for us to pursue all the theoretical considerations involved or to discuss the complications that may arise in practice. The open-hearth process, for example, is complicated by the considerable number of substances present that may enter into reactions, and the extent to which equilibrium is approached is greatly affected by the viscosity of the slag, by temperature change, and by the rates at which the substances may diffuse through the metal and the slag. Even when equilibrium is not attained, study of it is often valuable because there is shown the direction in which a reaction tends to go, the final limits it may reach, and the effect of changes in concentration, temperature, and pressure.

Mass Action.—When a charge of pig iron is blown in a Bessemer converter to remove the impurities from it, their oxidation takes place, in general, in the order of their affinities for oxygen. There is always, however, an unavoidable oxidation of iron, even though its affinity for oxygen is lower than that of the impurities. This is because the iron is present in much greater concentration, and accordingly its oxidation is said to be due to "mass action."

The example given above is an illustration of the obvious fact that the velocity of a reaction depends, other things being equal, on the number of contacts made per unit of time by the atoms or molecules which react. The important principle known as the *law of mass action* or the *mass law* goes beyond this simple qualitative relation and affords a basis for quantitative calculation. It is operative to some degree in all metallurgical processes that involve chemical change but can be used quantitatively only when operating conditions are such as to produce or approach equilibrium conditions. First formulated by C. M. Guldberg and P. Waage,[1] it may be stated in modern terms as follows:

The velocity of a reaction is proportional to the product of the activities of the reacting substances.

The "activity" represents the *effective* concentration of a substance and usually differs from the total concentration. It is a specifically defined property, but for most purposes it can be given in simple terms (in some cases only approximately). For a gas the activity is equal to its partial pressure. For an ideal solution the activity of the dissolved substance is equal to its molal concentration. For a solid (and also for a pure liquid) the activity is constant at a given temperature and is independent of the amount present.

Equilibrium Constants.—To make use of the mass law, consider the reversible reaction

$$A + B \rightleftarrows C + D,$$

and assume for illustration that the substances are present in ideal solutions having the concentrations $[A]$, $[B]$, $[C]$, and $[D]$ in mols per liter. From the mass law, the velocity of the reaction from left to right is proportional to $[A] \times [B]$ and that of the reaction from right to left to $[C] \times [D]$. Then, when there is no net change in either direction, *i.e.*, when the substances are in chemical equilibrium, $K_1[A] \times [B] = K_2[C] \times [D]$, or:

$$\frac{K_2}{K_1} = K = \frac{[C] \times [D]}{[A] \times [B]}, \tag{1}$$

where K is the *equilibrium constant* of the reaction. By convention the products are put in the numerator and the reactants in the denominator in Eq. (1).

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[1] "Études sur les affinités chimiques," Brogger & Christie, Christiania, 1867.

When the substances are not in equilibrium, as is usually the case during the carrying out of a metallurgical process, the velocity of the reaction in one direction or the other is proportional to the ratio of the products of the activities, so that increasing the concentration of the reactants or diminishing the concentration of the products (as by continuous escape or removal thereof) increases the rate of the *net* reaction accordingly. If a reaction takes place in a confined space, it cannot go to completion but approaches completion in proportion to the magnitude of K Often K is so large as to make the reaction complete for all practical purposes.

The value of K remains constant with change of concentration for a given group of substances in equilibrium under fixed surrounding conditions. If more of substance A is added, then B must decrease or C or D increase so as to keep K constant. K varies with temperature, however, and its numerical value depends on the units used In a reaction involving gases, K is customarily calculated with the partial pressures of the gases expressed in atmospheres and would have a different value if the pressures were in millimeters of mercury.

For a given value of K, the percentage completion of a reaction (percentage of the reactants converted into the products) may be obtained as shown in the following section

Calculation of the Percentage Completion of a Reversible Reaction and the Composition Reached at Equilibrium.—Let the reaction be represented by:

$$aA + bB + eE \rightleftarrows cC + dD + eE,$$

where a is the number of mols of substance A, b of substance B, etc., and E represents any inert gas or gases present (which will not enter into the reaction but will account for part of the total pressure) In equilibrium calculations the activities of all solids present as such in their standard states are unity (by definition), and hence these may be disregarded without affecting the solution of the problem. We shall therefore assume that A, B, C, and D are gases having the partial pressures p_A, p_B, p_C, and p_D. Then:

$$K = \frac{(p_C)^c \times (p_D)^d}{(p_A)^a \times (p_B)^b}. \tag{2}$$

Let the total pressure be P. Then at equilibrium the partial pressure of A will be that fraction of P represented by the number of mols of A present at equilibrium (denoted by the symbol n_A) divided by the total mols of $A + B + C + D + E$ present at equilibrium. Accordingly:

$$p_A = \frac{n_A}{n_A + n_B + n_C + n_D + n_E} \times P,$$

$$p_B = \frac{n_B}{n_A + n_B + n_C + n_D + n_E} \times P, \text{ etc.} \tag{3}$$

By substitution of Eq. (3) in Eq. (2):

$$K = \frac{(n_C)^c \times (n_D)^d}{(n_A)^a \times (n_B)^b} \times \left(\frac{P}{n_A + n_B + n_C + n_D + n_E}\right)^{(c+d)-(a+b)} \tag{4}$$

From this equation, if K is known for any reaction we may calculate for any total pressure P the percentage completion of the reaction at equilibrium. Let x be the completion expressed as a decimal giving the fraction of A that has been converted or consumed when equilibrium is reached. Then $n_C = xc$, $n_D = xd$, $n_A = (1 - x)a$, and $n_B = (1 - x)b$, so that:

$$K = \frac{(xc)^c \times (xd)^d}{(a - ax)^a \times (b - bx)^b} \times \left(\frac{P}{(1 - x)(a + b) + x(c + d) + e}\right)^{(c+d)-(a+b)} \tag{5}$$

The known values of K and P are substituted in this equation, which is then solved for x. (It is here assumed that the total amounts of A and B originally present were in the ratio $a:b$.)

Example 23

Cadmium is being produced by reducing its oxide with pure CO in a retort with only a small opening to maintain the pressure at 1 atm. Assume an initial temperature in the retort of 427°C. and a final temperature of 1027°C., each of these temperatures being maintained for a sufficiently long time for equilibrium to be reached. The equilibrium constant K for the reaction $CdO + CO = Cd(g) + CO_2$ has the value of 0.462 at 427° and 154.5 at 1027°.

Required. 1. The percentage completion of the reaction at equilibrium at each of the above temperatures, as represented by the percentage conversion of CO to CO_2.

2. The percentage of cadmium vapor (by volume) in the gas mixture at equilibrium at each temperature.

3. The percentage completion of the reaction at 427° if the CO in the retort were mixed with three-fifths its volume of nitrogen.

Solution. For this reaction in Eq. (5), $a = 1$, $b = 0$, $c = 1$, $d = 1$, and $e = 0$. $P = 1$ atm.

Then:

$$\frac{x^2}{1 - x} \times \frac{1}{(1 - x) + 2x} = 0.462, \text{ or } 154.5,$$

whence

$$x = 0.563, \text{ or } 56.5 \text{ per cent at } 427°,$$

and

$$0.998, \text{ or } 99.8 \text{ per cent at } 1027° \ (1)$$

$$\text{Per cent cadmium vapor} = \frac{0.563}{1.563} \times 100 = 36.0 \text{ per cent at } 427°,$$

and

$$\frac{0.998}{1.998} \times 100 = 49.95 \text{ per cent at } 1027° \ (2).$$

When the CO is mixed with three-fifths its volume of nitrogen, $e = 0.60a$. Then.

$$\frac{x^2}{1-x} \times \frac{1}{1-x+2x+0.6} = 0.462$$

$$1.462x^2 + 0.2772x - 0.7392 = 0.$$

$$x = 0.622, \text{ or } 62.2 \text{ per cent } (3).$$

This example illustrates the fact that dilution with an inert gas increases the degree of completion of the reaction when the reaction is one which results in an increase in the number of mols of gas. If the number of mols of gas were the same in the products as in the reactants, dilution would have no effect; and if the number of mols were decreased, the percentage completion would be decreased. A further consideration of the equation would show that addition of excess reactants would increase the degree of completion, while addition of reaction products to the initial reacting system would have the opposite effect.

If a similar calculation be applied to the reduction of FeO by CO, the result would hold only for a closed chamber or confined space, or for a time of contact sufficient to reach equilibrium, and would not apply quantitatively to the iron blast furnace, where the products of the reaction are rapidly removed. Nevertheless, the low value obtained for the degree of completion of the reaction at equilibrium would emphasize the need of maintaining a high concentration of CO in order to make the reaction ($FeO + CO \rightleftarrows Fe + CO_2$) proceed from left to right.

Equilibrium in the Open-hearth Process.—The problem here is one of equilibrium between substances in solution. In the metal bath, Fe is the solvent, and the assumption is made that the activities of the reacting substances and products are represented with sufficient accuracy by their concentrations. The substances of most importance include C, Mn, P, Si, their oxides, and FeO. Oxides formed by elimination of the elements from the steel may pass into the slag, and the concentrations of the products may thus be reduced by silicate formation and other reactions in the slag, so that the basicity of the slag becomes an important factor. Equilibrium constants have been determined for the principal reactions in the metal and in the slag by various investigators, using both laboratory experiments and actual furnace data, at various temperatures; but it is recognized that the assumptions necessary and variations in conditions cause considerable uncertainty in the values. The rate at which the reacting substances may be brought into contact depends on rates of diffusion and on stirring or motion in the furnace as well as on the viscosity of the metal and of the slag, and the latter in turn vary with composition and temperature. The exact mechanisms of the reactions, as determined by intermediate stages, are also important and uncertain. Data are being accumulated that throw light on some of these factors.

The reaction $FeO + C \rightleftarrows Fe + CO$ is regarded as the principal rate-determining reaction in the process, and much of the work done has centered in it. Here $K = \frac{[CO]}{[C][FeO]}$; and when the pressure of the CO is 1 atm., the value of the constant $K' = [C][FeO]$ becomes the determinant From values of K' there can be calculated the percentage of FeO necessary in the slag to reduce the carbon in the steel to a given point at a given temperature, or the amount of carbon there will be in the metal when the slag contains a given amount of FeO at a given temperature.

The same reactions apply in the deoxidation of steel. Here the reaction $Mn + FeO \rightleftarrows MnO + Fe$, in which $K = \frac{[MnO]}{[Mn][FeO]}$, is of particular importance.

S. Marshall and J. Chipman[1] have described a method for studying the equilibria between carbon and oxygen in liquid iron and CO and CO_2 and have determined the equilibrium constants in the range 1540 to 1700°C. for the following reactions:

$$\begin{aligned} C\ (\text{in Fe}) + CO_2 &= 2CO. \\ O\ (\text{in Fe}) + CO &= CO_2. \\ C\ (\text{in Fe}) + O\ (\text{in Fe}) &= CO. \end{aligned}$$

Study of the open-hearth process from this point of view began actively with the work of C. H. Herty, Jr., published in 1926. He and numerous others have continued to make important contributions.[2]

EQUILIBRIUM AND FREE-ENERGY CHANGE

Free-energy change in chemical reactions and its calculation is discussed in Chap. XXIV. It is desirable, however, to point out here the relation between the standard free-energy change (ΔF°) and the equilibrium constant K, which is given in the following equation:

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[1] "The Carbon-oxygen Equilibrium in Liquid Iron," *Trans. Am. Soc. Metals*, **30**, 695–746 (1942).

[2] For further information on this subject, reference may be made to *Carnegie Inst. Tech. Mining Met. Advisory Boards, Bulls* 68 and 69 in "The Physical Chemistry of Steel Making," Pittsburgh, 1934, and especially to papers in volumes of *Trans. Am. Inst. Mining Met. Eng.* (*Iron and Steel Division*) for the years 1926, 1928, 1929, 1930, 1931, 1935, 1940, and 1941.

$$\Delta F^\circ = -RT \ln K.^* \tag{6}$$

Here R is the gas constant (= 1.9885 cal. per degree centigrade), T is the absolute temperature at which the reaction takes place, and ΔF° is in calories per mol.†

From this equation it is seen that ΔF° as well as K is a measure of the extent to which a reaction will proceed to equilibrium. The signs in the equation result from the conventions adopted as to both ΔF and K. With the standard conventions, the larger the value of $-\Delta F^\circ$, *i.e.*, the greater the amount of free energy liberated, the greater the value of K, and vice versa. A reaction in which K is large and ΔF° has a large negative value can take place readily and go nearly to completion. When ΔF° has a large positive value, K is a small fraction. Note that, while K is based on velocities of reactions, it is itself only a ratio, a pure number; neither ΔF nor K is indicative of the velocity of a reaction. The statement that the reaction will take place readily does not mean that it necessarily proceeds at a high velocity; the rate of the reaction may be very low, especially at room temperature. ΔF° and K determine whether a reaction can be vigorous, how far it will go toward completion in a confined space, and, as between two or more possible reactions, which is most likely to predominate. At equilibrium, $\Delta F = 0$.

According to Berthelot's principle, the heat of a reaction (ΔH) was taken as a measure of equilibrium. Thus, liberation of a large amount of heat in a reaction was regarded as a large driving force; and the greater the value of $-\Delta H$, the more likely the reaction would be to occur. It is now known that this is not in general true, though it happens to be qualitatively true in the greater number of reactions. In general ΔF, not ΔH, is the measure of the driving force, and ΔF is determined by both ΔH and the heat capacities of the reacting substances and the products:[1]

$$\Delta F = \Delta H - T \int_0^T \frac{\Delta C_p \, dT}{T},$$

in which ΔC_p is the difference between the heat capacities of the products and of the reactants. Both ΔF and K are true measures of chemical affinity, while ΔH is not.

Obviously, both ΔF and K vary greatly with temperature.

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* If the reacting substances and products are not in their "standard states," Eq. (6) does not hold. The standard state for gases is a pressure of 1 atm

† An illustration of the use of this equation is given in Example 46, p. 380.

[1] See p. 375.

Whether a reaction will occur in the left-right or in the right-left direction is determined largely according to the following two principles:

1. A reaction is most likely to occur when the free-energy change has the maximum negative value, *i.e.*, the reaction will take place in the direction in which ΔF is negative.

2. A reaction occurs at the greatest velocity when the concentrations of the reactants as compared with the concentrations of the products is the greatest.

Le Châtelier's principle may also be applied in this connection. This law states that, if a system in equilibrium is subjected to an influence which upsets the equilibrium, the change will take place in such direction as to oppose the influence and tend to restore the equilibrium. According to this principle, raising the temperature will favor the direction in which a reaction is endothermic, while a lower temperature will favor an exothermic reaction. The effect of change of pressure on a reaction involving evolution of a gas or any change in volume can also be predicted in this way.

Problems

222. Among the proposed new methods for production of zinc is reduction with methane The reaction is.

$$ZnO + CH_4 = Zn(g) + CO + 2H_2.$$

The equilibrium constant for this reaction determined for 727°C. is 0.00308, and for 927°C it is 25.5

Required 1. The direction in which the reaction would predominate at each of these temperatures.

2 The percentage completion of the reaction taking place in a retort (*a*) at 727°, and (*b*) at 927°.

3 The percentage composition by volume of the gases in the retort at equilibrium at each temperature

223. The reaction $CO_2 + H_2 \rightleftarrows CO + H_2O$ was investigated by passing mixtures of CO_2 and H_2 over a catalyst at a high temperature (900°C).[1] The resulting gas was chilled quickly to room temperature by passage through a capillary and analyzed. In one experiment the partial pressures were as follows: $CO_2 = 0.2142$; $H_2 = 0.2549$; $CO = 0.2654$; $H_2O = 0.2654$ atm.

Required· 1. The value of the equilibrium constant.

2. The number of mols of H_2 present in an equilibrium mixture containing 22.72 mols of CO, 22.72 mols of H_2O, and 48.5 mols of CO_2

3. The percentage composition of the gases in this equilibrium mixture.

4. The percentage composition of the initial mixture of CO_2 and H_2 which will give the equilibrium composition of requirement 3.

224. The following two reactions occur in the roast-reaction process of producing lead:

$$(a)\ PbS(s) + 2PbO(s) = 3Pb(l) + SO_2.$$
$$(b)\ PbS(s) + PbSO_4(s) = 2Pb(l) + 2SO_2.$$

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[1] Problem taken from F. H. Getman and F. Daniels, "Outlines of Theoretical Chemistry," p 283. John Wiley & Sons, Inc., New York, 1937.

The equilibrium constants for these reactions have been determined as follows: For (*a*): $K = 0.0000936$ at 600°C. and 0.0310 at 800°C. For (*b*): $K = 4.2 \times 10^{-8}$ at 527°C. and 0.93 at 827°C. [Since the reactants are solids and no solution in the liquid lead is involved, the activities of these substances may be taken as unity, so that the partial pressure of the SO_2 (in atmospheres) alone determines K.]

Required: 1. The partial pressure of the SO_2 in reaction (*a*) at equilibrium, in millimeters of mercury, when the total pressure is 760 mm., at 600° and at 800°.

2. What pressure of SO_2, in millimeters of mercury, would prevent reaction (*b*) from taking place at 527° and at 827°?

225. For the reaction $FeO + CO = Fe(s) + CO_2$, the equilibrium constant at 1000°C. is 0.403.

Required: 1. The percentage completion of the reaction if allowed to reach equilibrium under normal atmospheric pressure, no gases other than CO and CO_2 being present.

2. Show that the percentage completion of this reaction will not be affected either by the presence of nitrogen in addition to the CO and CO_2 or by a change in the total pressure. For what type of reaction does this hold?

3. Find the number of mols of CO that must be present originally to cause reduction of 1 mol of Fe, and the volume of CO, in cubic meters at standard conditions, that must be supplied to produce 1,000 kg. of Fe when equilibrium is reached.

4. What volume of CO per 1,000 kg of Fe produced will be consumed in the reaction?

226. The standard free-energy equation for the reaction $2Ag + \frac{1}{2}O_2 = Ag_2O$ is as follows:

$$\Delta F^\circ = -7{,}240 - 1.0\,T \ln T + 21.95T$$

Required. 1. The equilibrium constants of the reaction at 0, 200, and 800°C.

2. In which direction would the reaction proceed under normal pressure at each of these temperatures?

227. Given the reaction $2CuO(s) + Cu_2S(s) = 6Cu(s) + SO_2$; $\Delta F^\circ = 34{,}480 + 9.37T \ln T + 0.0063T^2 - 105.212T$.

Required: 1. The equilibrium constant for the reaction at 127°C.

2. The temperature at which equilibrium would exist, disregarding changes of state in the reacting substances.

CHAPTER XIII

DRYING AND CALCINING

The term "drying" is applied to the removal of water from a material, whether a solid, liquid, or gas, and whether the water be present as liquid moisture, water vapor, or chemically combined water. The nature of the process of drying, however, differs with these different circumstances.

Consider first the case of a solid, for example, ore, containing (*i.e.*, mixed with) liquid water that causes it to be "wet." The presence of the water when the material is charged into a smelting furnace may impose an additional burden on the furnace thermally, since heat will be absorbed in evaporating the water. This may lower the temperature in the furnace or may increase the time required for fusion of the charge. Sometimes, as in a copper converter, there may be a violent reaction from addition of wet material. Mechanical difficulties in handling or charging, particularly in automatic devices, may result from wet, sticky material. Preliminary drying of ore or flux is therefore often desirable. Since, however, removal of water will take place in the smelting furnace, the metallurgist must decide whether the additional cost imposed on the smelting operation by the presence of moisture is greater or less than the cost of separate drying.

The removal of water from ore is accomplished by vaporizing it. The process of causing the water to pass from liquid to vapor consists essentially in raising the vapor pressure of the water above the opposing pressure of water vapor above it or around it, thus upsetting the previous condition of equilibrium. One way of doing this is to heat the water to its boiling point, but this operation is required only in the case of a nearly closed container affording no means for the water vapor formed to be carried away. In this case the water vapor would be in contact only with water vapor, the pressure of the latter would be the total pressure of the surroundings (normally in the neighborhood of 760 mm.), and the water would have to be heated to the temperature at which its vapor pressure equaled or exceeded 760 mm. But if the water vapor is carried away nearly as fast as it forms, as by a draft of air, the opposing *water vapor pressure* is maintained at a low value and water evaporates correspondingly. The *maximum* volume of water vapor that can be carried away is, in accordance with Dalton's law of partial pressures, equal to the vapor pressure of water at the existing temperature divided by the pressure of the air in contact with it, multiplied by the volume of the air:

$$\frac{P_{H_2O}}{P_{air}} = \frac{V_{H_2O}}{V_{air}},$$

whence

$$V_{H_2O} = \frac{P_{H_2O}}{P_{air}} \times V_{air}.$$

Actually the volume of water vapor removed will be less than this maximum, because the actual pressure of the water vapor in the air-water vapor mixture will be less than the maximum vapor pressure of water; *i.e.*, the air will not be *saturated* with water vapor. But it is obvious that the same amount of water removal will result from a low pressure of 1 mm. and a high volume of 10,000 cu. ft. as from the proportionately higher pressure and lower volume, 10 mm. and 1,000 cu. ft.; in each case the amount of water vapor would be $\frac{10,000}{760}$ cu. ft.

One other essential factor must be provided for in the evaporation of the water, *viz.*, supplying the necessary heat. The main heat requirement is the latent heat of vaporization. No particular temperature need be maintained to supply the heat, so long as the temperature of the source is greater than the temperature of the particles of water being evaporated, so that heat will flow to them. But the greater this heat gradient, the more rapidly will heat be taken up by the water and the greater will be the amount of water evaporated in a given time. Therefore a high temperature is advantageous in drying. The supply of heat must also take care of losses, including the heat carried out in the gases, as well as radiation and conduction. These losses increase with the temperature. This, with the prevention of fusion and possibly of certain chemical reactions, imposes a limit on the temperature.

Example 24

Iron ore is dried by passing hot flue gases upward through a furnace through which the ore passes slowly downward. The gases entering amount to 7,200 cu. m. per hour (standard conditions), analyzing:

	Per Cent
CO_2	10.6
O_2	6.5
N_2	74.8
H_2O	8.1

The ore contains 90 per cent Fe_2O_3 and 10 per cent SiO_2 when dry, and the wet ore carries 18 per cent moisture, all of which is removed by the drier.

The ore enters at 20°C. and is discharged at 200°C. The gases enter at 450°C. and leave at 90°C., being one-fourth saturated with water vapor on leaving. The barometric pressure is 740 mm.

Required: 1. The tons of wet ore dried, per 8-hr. shift.

2. A heat balance of the drier, per ton of wet ore.

Solution: The gases entering in 8 hr. contain 0.081 × 8 × 7,200 = 4,660 cu. m. of H_2O.

Vapor pressure of H_2O in gases leaving at 90°C. = $\frac{1}{4}$ × 526 mm. = 131 mm. Volume of these gases without H_2O = 8 × 7,200 − 4,660 = 52,940 cu. m. Volume of H_2O in them when leaving = $\frac{131}{740 - 131} \times 52{,}940$ = 11,390 cu. m.

H_2O removed from ore = 11,390 − 4,660 = 6,730 cu. m. = 5,410 kg.

Tons of ore dried = $\frac{5{,}410}{180}$ = 30.0 (1)

Heat entering:

In ore:

In Fe_2O_3 = 0.90 × 820 × 0.15 × 20 = 2,200 Cal.
In SiO_2 = 0.10 × 820 × 0.17 × 20 = 300
In H_2O = 180 × 20 = 3,600
Total = 6,100 Cal.

In gases: Volume of gases per ton of wet ore = $\frac{8 \times 7{,}200}{30}$ = 1,920 cu. m.

Heat in gases:

CO_2 = 0.106 × 1,920(0.406 + 0.00009 × 450)450 = 40,900 Cal.
O_2 and N_2 = 0.813 × 1,920(0.302 + 0.000022 × 450)450 = 219,200
H_2O = 0.081 × 1,920(0.373 + 0.00005 × 450)450 = 27,700
Total = 287,800 Cal.

Heat required to evaporate H_2O (from 20°) = 180 × 586 = 105,500 Cal.

Heat in gases leaving:

CO_2 = 0.106 × 1,920(0.406 + 0.00009 × 90)90 = 7,600 Cal.
O_2 and N_2 = 0.813 × 1,920(0.302 + 0.000022 × 90)90 = 42,700
H_2O = $\frac{11{,}390}{30}$(0.373 + 0.00005 × 90)90 = 12,900
Total = 63,200 Cal.

Heat in ore leaving:

Fe_2O_3 = 738 × 0.18 × 200 = 26,600 Cal.
SiO_2 = 82 × 0.20 × 200 = 3,300
Total = 29,900 Cal.

HEAT BALANCE OF DRIER

Heat entering, Calories		Heat distributed, Calories	
In gases	287,800	Used in evaporation	105,500
In ore	6,100	Lost in gases	63,200
		Lost in ore	29,900
		Radiation, etc.	95,300
Total	293,900	Total	293,900

If the material to be dried contains chemically combined water, as in hydrates or water of crystallization, the temperature must be high enough to break up the chemical combination. This also absorbs additional heat. An elaborate drying operation, especially where combined water is removed, is often called "dehydrating."

Drying of Gases.—Drying of gases is usually done by absorption of the water vapor by some dehydrating agent through which the mixture is passed. The agent may be sulphuric acid, calcium chloride, silica gel, or some other material. Usually chemical combination between the water and the drying agent is involved, and in some respects, therefore, the process is the reverse of that just considered. Ordinary or low temperatures are employed. The governing principle is again that of equilibrium between two opposing tendencies. Such a process may be studied from another angle by means of the law of mass action and the principles of chemical equilibrium. Additional consideration is given to vapor pressure and to chemical equilibrium in Chaps. XII, XXII, and XXIII.

Refrigeration is another method of removing water vapor from a mixture of gases. The temperature of the mixture is lowered to a point where the maximum vapor pressure of water is very low and all vapor present in excess of that corresponding to this saturation pressure must condense. Results achievable by this method may readily be computed. Practically it is difficult to cool large volumes of gas efficiently to temperatures required for sufficient dehydration, usually close to 0°C. It is evident that this process is physically the reverse of evaporation, considered above. Some applications of this method have been made in practice, as in Gayley's process of drying the blast for the iron blast furnace and in removing water vapor from gases to be used in controlled-atmosphere furnaces for heat-treating.

Roasting and Calcining.—Drying has been discussed at some length because the same principles apply in any metallurgical or chemical process where vapor or gas is formed by thermochemical action. Liberation of SO_2 in roasting and the reduction of oxides by carbon are examples. The formation of sulphates in roasting can be studied profitably from this angle, the question being one of equilibrium in a reaction[1] such as

$$MSO_4 \rightleftarrows MO + SO_3.$$

Calcining, which is exemplified by the decomposition of carbonates with expelling of CO_2, will be only briefly mentioned here. From thermodynamic principles it is possible to determine the constants in an expression of the form $\log p = -\frac{A}{T} + B$ giving the relations between

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[1] The reactions for decomposition of sulphates are usually not so simple as this; frequently a sulphate such as $MO.MSO_4$ is formed.

p and T, in which p is the pressure of gas evolved at any temperature T, for example, the pressure of CO_2 in the reaction

$$CaCO_3 = CaO + CO_2.$$

This question is discussed and illustrated in Chap. XXIII.

Problems

228. Iron ore is dried by hot flue gases passing through a revolving cylindrical kiln through which the ore passes slowly downward. The flue gases are obtained from a near-by furnace burning 0.6 metric ton of coal per hour. The coal analyzes as follows:

	Per Cent
C	74.2
H	7.2
O	7.0
H_2O	2.4
Ash	9.2

The ashes from this furnace are 21 per cent carbon, and air 50 per cent in excess of the theoretical requirement enters the flue gases. The air is at 15°C., 740 mm., and three-fourths saturated with water vapor.

The kiln is 1.8 m. in diameter. The flue gases enter it at 480°C., 720 mm., and leave at 80°C., one-third saturated with water vapor.

The wet ore carries 22 per cent H_2O, all of which is removed by the drier.

Required: 1. Per kilogram of coal, the cubic meters of flue gas, measured at standard conditions; and the grams of H_2O contained per cubic meter.

2. The velocity of the flue gases entering the drier, in meters per minute.

3. The tons of ore dried per hour.

229. Products of combustion from a furnace have a temperature of 800°F. and analyze CO_2, 10 per cent, N_2, 75; O_2, 6; H_2O, 9. These flue gases, amounting to 215 cu. ft. (standard conditions) per pound of coal burned in the furnace, are used in a drier to dry iron ore carrying 20 per cent H_2O. The gases leave the drier at 175°F., one-third saturated with water vapor. The dried ore is 85 per cent Fe_2O_3 and 15 per cent SiO_2 and leaves the drier at 300°F. Atmospheric temperature is 70°; barometer, 30.2 in.

Required: 1. The tons of ore dried, per ton of coal burned.

2. The heat content of the gases and ore entering the drier, in B.t.u.

3. The heat content of the gases and ore leaving the drier.

4. A heat balance of the operation of the drier.

5. The thermal efficiency of the drying operation.

230. An iron ore from the Cleveland district, England, has the following composition:

	Per Cent
$FeCO_3$	58.1
SiO_2	11.5
$CaCO_3$	11.7
Al_2O_3	10.5
H_2O	8.2

It is calcined in a kiln from which the gases issue at a temperature of 375°C. Barometric pressure, 742 mm. The kiln is fired with coke containing 84 per cent C, 13 ash, 3 H_2O, and just enough air is used to burn it completely. 80 kg. of coke is used per ton of ore.

Required: 1. The volume of air used, at standard conditions, per ton of ore.

2. The volume of the gases issuing from the kiln, at standard conditions

3. Their volume at the conditions given

4. The percentage, grams per cubic meter, and partial pressure of the water vapor in the gases.

CHAPTER XIV

ROASTING AND SINTERING

Roasting in metallurgy is essentially oxidation. While it may have several objects, usually the principal one is removal of all or part of the sulphur from the ore. The sulphur removed forms SO_2, with perhaps a little SO_3, and passes off in the gases. Some of the sulphur, however, is often converted to sulphates and remains in the roasted ore. As the roasting action is usually incomplete, often purposely so, especially in the case of copper ores, some of the sulphides remain unattacked and are present in the roasted ore in the same form as they existed in the raw ore. When FeS_2 is present, as is very often the case, all of this compound will lose one atom of sulphur because it is easily decomposed:

$$FeS_2 = FeS + S$$

Most of the resulting FeS will be oxidized, chiefly to Fe_2O_3.

Roasting requires free access of air in amounts largely in excess of those theoretically required by the roasting reactions, in order that each particle of ore may have sufficient contact with oxygen of the air. Stirring of the ore to expose all surfaces is another requirement in this connection. The roasting of some ores, particularly zinc blende, is rendered more exacting because the ore particles become coated with an impervious layer of oxide (in this case, ZnO). Such ores require finer grinding before roasting and more careful application of proper roasting conditions.

In the case of elements forming more than one stable oxide, as FeO, Fe_3O_4, and Fe_2O_3 for iron and MnO, Mn_2O_3, and MnO_2 for manganese, smelting produces the lowest oxide, which then combines with SiO_2 and other compounds to form slag; but roasting results in one of the higher oxides. Fe_2O_3, often with a relatively small amount of Fe_3O_4, is the usual result of roasting iron sulphides.

In some cases, as in roasting sulphide of antimony, the temperature and the amount of air supplied may be factors that determine which oxide is formed. Conditions may be regulated to produce either the more stable Sb_2O_4 or the more volatile Sb_2O_3.

Sintering is a process of heating a finely divided material to a point where it softens enough to agglomerate, or form a cake, but without fusion. Sintering often accompanies roasting in the variety of roasting known as "blast roasting," and the combined process is often called "roast sintering." However, sintering may be done when no roasting is desired, as in sintering oxide ores of iron. Sintering is usually accomplished with the Dwight-Lloyd machine.

There is no fusion or formation of slag in roasting. The only products to be considered in calculation, therefore, are the roasted ore, often called "calcines," and the gases. The charge consists primarily of the raw ore, but other materials may be mixed with it, especially in blast roasting. Any kind of fuel may be used, and, in sintering, some of the fuel may be mixed with the charge. In some cases roasting may be carried on without fuel after ignition, since the oxidation of the ore generates a large amount of heat. A heat balance sheet may be employed to study the possibility of this "autoroasting" with any given ore.

Two types of problems on roasting will now be illustrated. The first of these deals with the calculation of the composition of the roasted product from a given raw ore and determination of the amount of air used in excess of the theoretical requirement when the composition of the roaster gases is known. The composition of the roasted ore will depend somewhat on the conditions, so that it is necessary either to have some information regarding what compounds are formed or to make certain assumptions regarding them.

Example 25

Copper ore roasted in McDougall furnaces at Great Falls, Mont., had the following composition (dry analysis):

	Per Cent		Per Cent
Cu	8.8	S	36.6
SiO_2	19.0	Al_2O_3	5.6
Fe	29.7	CaO	0.3

The wet ore carried 9.0 per cent H_2O.

The ore was roasted down to a sulphur content of 6.8 per cent, dry. Assume that 5 per cent of the copper forms CuO and the remainder is unoxidized as Cu_2S. Assume that the iron oxidized forms Fe_2O_3 and the rest of the iron is present as FeS.

The gases issuing from the furnace analyze (dry):

	Per Cent
SO_2	2.61
SO_3	0.27
CO_2	0.12
O_2	17.20
N_2	79.80

Required: 1. The weight and proximate analysis (*i.e.*, according to compounds) of the roasted product from 1,000 kg. of raw ore, dry weight (or 1,100 kg. of wet ore).

2. The volume of the gases, including H_2O, per 1,000 kg. of raw ore, dry weight.

3. The volume of air supplied and the percentage excess over that theoretically required for the roasting reactions.

Solution:

$0.05 \times 88 = 4.4$ kg. of Cu forms CuO. $4.4 \times {}^{80}\!/_{64} = 5.5$ kg. CuO.

$88 - 4.4 = 83.6$ kg. of Cu as Cu_2S. $83.6 \times {}^{160}\!/_{128} = 104.5$ kg. Cu_2S.

The rest of the S will be in FeS and will determine the weight of FeS. The S used in Cu_2S is $104.5 - 83.6 = 20.9$ kg. The total S is 6.8 per cent of the *roasted ore*, but the weight of the roasted ore is not known: it is being sought. One method of procedure would be to assume some weight for the roasted ore, say 900 kg., later correcting the assumption (the so-called "method of approximations"). This procedure will be indicated, and then the usually preferable algebraic method will be followed through

Assuming the weight of the roasted ore to be 900 kg., $0.068 \times 900 = 61.2$ kg. of S. $61.2 - 20.9 = 40.3$ kg. of S in FeS. $^{88}/_{32} \times 40.3 = 110.8$ kg. FeS. Fe in this $= 110.8 - 40.3 = 70.5$ kg. Fe as $Fe_2O_3 = 297 - 70.5 = 226.5$ kg. $Fe_2O_3 = 226.5 \times {}^{160}/_{112} = 324$ kg.

SiO_2, Al_2O_3, and CaO are not affected by roasting. The total weight of the roasted ore is now $5.5 + 104.5 + 110.8 + 324 + 190 + 56 + 3 = 794$ kg

This result is inaccurate because it is based on the assumption that the weight was 900 kg instead of the closer value of 794 kg Now go back and use 794 instead of 900, and follow the calculation through again. The new result should be approximately correct; a third approximation would have to be made to ensure the best result.

The algebraic method is as follows:

Let x = the weight of the roasted ore

Then $0.068x$ = kilograms of S in it, and $0.068x - 20.9$ is the S in FeS. $FeS = {}^{88}/_{32}(0.068x - 20.9) = 0.187x - 57.5$. Fe in this $= 0.119x - 36.6$ Fe as $Fe_2O_3 = 297 - (0.119x - 36.6) = 333.6 - 0.119x$. $Fe_2O_3 = {}^{160}/_{112}(333.6 - 0.119x) = 477 - 0.170x$.

The sum of all the compounds in the roasted ore will equal x, which was taken as the weight of roasted ore:

$$5.5 + 104.5 + (0.187x - 57.5) + (477 - 0.170x) + 190 + 56 + 3 = x,$$

whence

$$
\begin{aligned}
x &= 792 \text{ kg. } (1). \\
CuO &= 5.5 \text{ kg} = 0.7 \text{ per cent} \\
Cu_2S &= 104.5 = 13.2 \\
FeS = 0.187x - 57.5 &= 90.5 = 11.4 \\
Fe_2O_3 = 447 - 0.170x &= 342.5 = 43.2 \\
SiO_2 &= 190.0 = 24.0 \\
Al_2O_3 &= 56.0 = 7.1 \\
CaO &= 3.0 = 0.4
\end{aligned}
$$

Now that the amount of sulphur entering the gases is known, the volume of the gases may be calculated from their sulphur content The gases contain 2.88 per cent $SO_2 + SO_3$, each of which contains 32 kg of S in 22.4 cu m. of gas

$$\frac{32}{22.4} \times 0.0288 = 0.0411 \text{ kg of S in each cubic meter of gas}$$

The total weight of sulphur entering the gases is $366 - (0.068 \times 792) = 312.2$ kg

$$\frac{312.2}{0.0411} = 7{,}610 \text{ cu. m. of gases, dry.}$$

Added to this is $1{,}100 - 1{,}000 = 100$ kg. of H_2O, or 124 cu m Total volume of wet gases = 7,734 cu. m. (2)

$$0.798 \times 7{,}610 = 6{,}070 \text{ cu. m. of } N_2 \text{ in gases.}$$

$$\frac{6{,}070}{0.79} = 7{,}690 \text{ cu. m. of air supplied (3).}$$

The air theoretically required is represented by the O in CuO, Fe_2O_3, SO_2, and SO_3

$$
\begin{aligned}
&\text{O in CuO} = 5.5 - 4.4 = 1.1 \text{ kg.} &&= 0.8 \text{ cu. m} \\
&\text{O in } Fe_2O_3 = {}^{48}/_{160} \times 342.5 = 102.7 \text{ kg.} &&= 71.9 \\
&\text{O in } SO_2 = 0.0261 \times 7{,}610 &&= 198.5 \\
&\text{O in } SO_3 = {}^{3}/_{2} \times 0.0027 \times 7{,}610 &&= \underline{30.8} \\
&\text{Total} &&= 302.0 \text{ cu m}
\end{aligned}
$$

$$\frac{302}{0.21} = 1{,}438 \text{ cu. m. of air required}$$

$$7{,}690 - 1{,}438 = 6{,}252 \text{ cu. m. excess.}$$

$$\frac{6{,}252}{1{,}438} = 435 \text{ per cent excess (3).}$$

The volume of excess air may also be determined from the free oxygen content of the gases

$$O_2 \text{ in gases} = 0.172 \times 7{,}610 = 1{,}309 \text{ cu. m.}$$

$$\frac{1{,}309}{0.21} = 6{,}233 \text{ cu. m. excess air}$$

$$7{,}690 - 6{,}233 = 1{,}457 \text{ cu. m. required air.}$$

$$\frac{6{,}233}{1{,}457} = 427 \text{ per cent excess (3).}$$

Heat Balance.—The heat balance of a roasting operation will now be taken up, using as an example a Dwight-Lloyd machine sintering lead ore. Limestone was added to the charge of the machine, and much depends in the heat balance on whether or not the $CaCO_3$ was broken up into CaO and CO_2. Whether or not this occurred could be determined by an examination of the product. It will be assumed here that half the $CaCO_3$ was decomposed and half remained unaffected. The disposition of the gases from the igniter is also an uncertain factor in the Dwight-Lloyd machine, and an assumption will have to be made regarding the proportion of these gases drawn into the suction box and the proportion escaping into the air. A large portion of the heat of the igniter also escapes without being utilized. This loss will simply be counted as part of the loss by radiation, convection, and conduction, which will be figured by difference as a single item.

Example 26

A Dwight-Lloyd sintering machine receives a mixture of:

100 parts of lead ore, containing 60 per cent PbS, 4 FeS_2, 36 SiO_2.
10 parts of silver ore, containing 4.5 per cent PbS, 0.5 Ag_2S, 95 SiO_2.
20 parts of spathic iron ore ($FeCO_3$)
25 parts of limestone ($CaCO_3$).

The charge is moistened with water equal to 10 per cent of its weight.

Assume that all the $FeCO_3$ and one-half the $CaCO_3$ are decomposed. The roast eliminates four-fifths of the sulphur from the charge. The gases from the suction box analyze 6.0 per cent SO_2, dry analysis. A large part of the PbO formed unites with the SiO_2 to form lead silicate. Assume that this combination liberates 200 Cal. per kilogram of SiO_2.

The gases enter the suction box at an average temperature of 300°C. The sinter is discharged at 450°C. Specific heat of the sinter, 0.20.

For igniting the charge there is used 10 kg. of oil per ton of dry charge. The calorific power of the oil is 10,000. Assume that the oil is 85 per cent C and 15 per cent H and that one-half the gases resulting from its combustion enter the suction box.

Required: 1. A charge balance sheet of the machine, based on 1,000 kg. of dry charge.

2. A heat balance of the operation.

Solution: The 1,000-kg charge would be divided as follows:

Lead ore = $^{100}/_{155} \times 1{,}000 = 645$ kg
Silver ore = $^{10}/_{155} \times 1{,}000 = 65$
$FeCO_3$ = $^{20}/_{155} \times 1{,}000 = 129$
$CaCO_3$ = $^{25}/_{155} \times 1{,}000 = 161$

The only feature of the charge balance sheet that may require explanation is the determination of the amount of air used. This problem must be approached from the fact that the gases contain 6 per cent SO_2. The procedure is as follows:

The total sulphur content of the charge is:

In lead ore: $(^{32}/_{239} \times 0.60 \times 645) + (^{64}/_{120} \times 0.04 \times 645) = 65.5$ kg
In silver ore: $(^{32}/_{239} \times 0.045 \times 65) + (^{32}/_{248} \times 0.005 \times 65) = 0.4$
Total = 65.9 kg.

Sulphur in gases = $0.80 \times 65.9 = 52.7$ kg

$$SO_2 \text{ in gases} = \frac{22.4}{32} \times 52.7 = 36.9 \text{ cu. m.}$$

$$\text{Volume of gases} = \frac{36.9}{0.06} = 615 \text{ cu. m (dry)}$$

O_2 used for SO_2 = 36.9 cu. m

O_2 used for PbO = $^{16}/_{239}(0.60 \times 645 + 0.045 \times 65) = 26.1$ kg. = 18.4 cu. m.

O_2 used for Fe_2O_3 = $^{48}/_{112} \times {}^{56}/_{120}(0.04 \times 645) = 5.2$ kg = 3.6 cu. m.

CHARGE BALANCE, DWIGHT-LLOYD MACHINE
(Per 1,000 kg. of dry charge)

Charge		Sinter		Gases (suction box)	
Lead Ore (645):					
PbS =	387	Pb =	335	S =	52
FeS_2 =	26	Fe =	12	S =	14
SiO_2 =	232	SiO_2 =	232		
Silver Ore (65):					
PbS =	3	Pb =	3	S =	0
Ag_2S =	0.3	Ag =	0.3	S =	0
SiO_2 =	61.7	SiO_2 =	61.7		
$FeCO_3$ =	129	FeO =	80	CO_2 =	49
$CaCO_3$ =	161	$CaCO_3$ = CaO =	80.5 45	CO_2 =	35.5
H_2O =	100			H_2O =	100
Oil (one-half of 10):					
C =	4.3			C =	4.3
H =	0.7			H =	0.7
Air (774):					
N =	595			N =	595
O =	179	O =	31	O =	148
Total =	1,879		880.5		998.5

$$\text{One-half of } O_2 \text{ used for oil} = \frac{1}{2}\left(\frac{22.4}{12} \times 0.85 \times 10 + \frac{22.4}{4} \times 0.15 \times 10\right) = 12.2 \text{ cu. m.}$$

Total required oxygen = 71.1 cu. m.

$$\text{Nitrogen accompanying this} = \frac{71.1}{0.21} \times 0.79 = 267 \text{ cu. m.}$$

CO_2 from combustion of oil = $\frac{1}{2}(\frac{44}{12} \times 0.85 \times 10)$ = 15.6 kg.

CO_2 from $FeCO_3$ = $\frac{44}{116} \times 129$ = 49.0

CO_2 from ½ of $CaCO_3$ = $\frac{44}{100} \times 80.5$ = 35.4

Total CO_2 = 100.0 kg. = 51 cu. m.

Total volume of dry gases without excess air = 37 + 267 + 51 = 355 cu. m.

Volume of excess air = 615 − 355 = 260 cu. m.

Total volume of air = 260 + 71 + 267 = 598 cu. m. = 774 kg.

The charge balance may be given as shown on page 231, without further explanation.

HEAT BALANCE, DWIGHT-LLOYD MACHINE

		Cal.	Per cent
Heat of combustion of oil	= 10 × 10,000	= 100,000 Cal.	= 24.6 per cent
Oxidation of S to SO_2	= 64 × 2,212	= 141,500	= 34.7
Oxidation of Pb to PbO	= 338 × 253	= 85,600	= 21.0
Oxidation of Fe to Fe_2O_3	= 12 × 1,777	= 21,300	= 5.2
Formation of lead silicate	= 294 × 200	= 58,800	= 14.5
Total heat available		= 407,200 Cal.	= 100.0 per cent
Decomposition of PbS	= 338 × 107	= 36,200 Cal.	
Decomposition of FeS_2	= 12 × 636	= 7,600	
Decomposition of $FeCO_3$	= 80 × 196	= 15,700	
Decomposition of $CaCO_3$	= 45 × 773	= 34,800	
Total heat absorbed in decomposition		= 94,300 Cal.	= 23.2 per cent
Evaporation of water	= 100 × 586	= 58,600	= 14.4
Sensible heat in sinter	= 800 × 0.20 × 450	= 79,200	= 19.4
Sensible heat in gases (see below)		= 74,600	= 18.3
Loss by radiation, etc. (by difference)		= 100,500	= 24.7
Total heat distributed		= 407,200 Cal.	= 100.0 per cent

Heat in gases.

$SO_2 + CO_2$ = $88(0.406 + 0.00009 \times 300)300$ = 11,400 Cal.

H_2O = $124(0.373 + 0.00005 \times 300)300$ = 14,400

$O_2 + N_2$ = $527(0.302 + 0.000022 \times 300)300$ = 48,800

Total = 74,600 Cal.

Problem 351 in Chap. XXI on Transfer of Heat deals with the rate at which zinc sulphide must be roasted in order to maintain a given temperature under certain assumed conditions.

Problems

231. A copper ore contains 20 per cent Cu_2S, 40 FeS_2, 30 SiO_2, 10 H_2O. It is roasted, fuel oil equal to 5 per cent of the weight of the ore charged being used. The gases from the combustion mix with the gases from the roasting reactions and are carried off through a flue. The sulphur passes off as SO_2. The roasted ore consists entirely of CuO, Fe_2O_3, and SiO_2. Air is used 100 per cent in excess of the theoretical requirement for roasting and combustion. The oil is 85 per cent C and 15 per cent H.

Required: 1. The cubic meters of air used for a metric ton of ore.

2. The weight of the roasted ore.

3. The grams of H_2O contained in each cubic meter of the flue gases.

232. The following data are taken from a multiple-hearth roasting furnace of the Anaconda Copper Mining Company:

	Raw Ore, Per Cent	Roasted Ore, Per Cent
Cu	8.8	11.1
SiO_2	19.0	24.0
Fe	29.7	37.6
S	36.9	10.0
Al_2O_3	5.3	6.7
CaO	0.3	0.4

Assume that the balance of the roasted ore is oxygen, also, that the copper in the roasted ore is entirely as Cu_2S, while the iron is partly as Fe_2O_3 and partly as Fe_3O_4.

The air used amounts to 7,046 cu. m per ton of ore; 4.54 kg. of carbon is burned as fuel with each ton of ore. Of the sulphur oxidized, 90 per cent goes to SO_2 and 10 per cent to SO_3.

Required: 1. The weight of the roasted ore, per ton of raw ore.

2. The proximate analysis of the roasted ore.

3. The percentage elimination of the sulphur.

4. The volume and percentage composition of the gases.

5. The percentage of excess air used, compared with the total theoretical requirement for burning the fuel and roasting the ore.

233. The gases from a roasting furnace were analyzed and found to contain:

	Per Cent
CO_2	1.8
SO_2	7.2
H_2O	0.6
N_2	80.1
O_2	10.3

The ore before roasting contained 10 per cent Cu, 34 Fe, 14 SiO_2, 42 S. Four-fifths of the sulphur is removed by the operation, and 50 tons of ore is charged per day. The fuel is coal containing 76 per cent carbon. The ore and fuel are separate, but the resulting gases mix.

Required: 1. The weight of roasted ore, per day, assuming it to contain only Cu_2S, FeS, Fe_2O_3, and SiO_2.

2. The cubic meters of gases, per day.

3. The amount of fuel used, expressed as percentage of the ore.

4. The percentage of excess air used over that theoretically required for combustion and roasting.

5. The ratio of air required theoretically for roasting to that required theoretically for combustion of the fuel.

234. A Wedge mechanical furnace roasts daily without the use of outside fuel 40 metric tons of copper concentrates carrying 25 per cent Cu_2S, 50 FeS_2, 17 SiO_2, and 8 H_2O, reducing the sulphur in the roasted product to 6 per cent. The roasted material will contain SiO_2, Cu_2S, Fe_2O_3, and CuO.

The furnace gases leave the furnace at 300°C. The roasted material is discharged at 400°C. Assume that the air and the concentrates enter at 0°C. The volume of air used is 150 per cent in excess of the theoretical requirement.

Required: 1. The weight of the roasted product, per day.

2. The volume of air used, per ton of ore.

3. The volume of the gases, per ton of ore.

4. A heat balance of the furnace, per day.

235. Copper concentrates are roasted in a Wedge mechanical furnace. The concentrates are composed as follows:

	Per Cent
Chalcopyrite	32
Chalcocite	7
Pyrite	35
Silica	18
Moisture	8

Assume that all the iron is oxidized to Fe_2O_3 and one-half the copper to CuO, the remaining copper being Cu_2S.

The furnace gases analyze 12 per cent O_2 and leave the furnace at 400°C. The roasted ore is discharged at 500°C. Assume 0°C as the entering temperature for the air and concentrates. No fuel is used.

Required: 1. The weight of roasted ore, per ton of concentrates charged.

2. The percentage of sulphur in the roasted ore, and the percentage of the original weight of sulphur eliminated.

3. The volume of air used, per ton of concentrates.

4. The percentage of excess air above the theoretical requirement.

5. The percentage composition of the gases.

6. A charge balance sheet of the furnace.

7. A heat balance sheet of the furnace.

236. A lead ore contains 70 per cent PbS, 10 $CaCO_3$, 15 SiO_2, 5 H_2O. It is roasted, using as fuel coke equal to 10 per cent of the weight of the ore charged. The gases from the combustion mix with the gases from the roasting reactions and are carried off through a flue. The sulphur passes off as SO_2. The roasted ore consists entirely of PbO, CaO, and SiO_2. Air is used 100 per cent in excess of the theoretical requirement for roasting and combustion. The coke is 90 per cent carbon and 10 per cent ash.

Required: 1. The cubic meters of air used, per metric ton of ore.

2. The weight of the roasted ore.

3. The percentage composition of the flue gases.

237. A lead roasting furnace roasts the following ore mixture down to a sulphur content of 4 per cent in the roasted ore:

Galena Concentrates, 100 Parts	Per Cent	Spathic Iron Ore, 10 Parts	Per Cent	Limestone, 20 Parts	Per Cent
PbS	92	$FeCO_3$	80	$CaCO_3$	96
SiO_2	8	SiO_2	20	SiO_2	4

To the mixture with a dry analysis as above, there is added before roasting enough water to make the moisture content 6 per cent of the dry weight. The carbonates are decomposed, liberating all the CO_2, and the PbS oxidized forms PbO and SO_2.

No fuel is used. The gases passing out of the roaster contain 3.6 per cent SO_2.

Required: 1. The weight of roasted ore made, per ton of dry ore mixture.

2. The volume of air theoretically required.

3. The percentage excess air used.

4. The net heat generated by the roasting process.

238. At the works of the International Smelting Company, Tooele, Utah, the charge to the Dwight-Lloyd machines totaled approximately as follows (dry analysis):

	Per Cent	
SiO_2	24.4	
$CaCO_3$	7.1	
Fe	33.1	(as FeS_2 and Fe_2O_3)
S	11.3	(as FeS_2 and PbS)

It was moistened with water equal to 8.6 per cent of the dry ore. It was roasted down to a sinter carrying 2.8 per cent S, all as FeS, the balance of the iron being as Fe_2O_3, the lime as CaO, and the lead as PbO. Neglect loss in dust and fume.

The charge was ignited by a burner using 10 kg. of oil per ton of ore. Assume the oil to be 85 per cent C and 15 per cent H. Assume that one-half the products of combustion of the oil were drawn into the suction box.

The gases drawn into the suction box amounted to 1,650 cu. m. (standard conditions) per ton of dry charge.

Required. 1. The percentage of lead in the dry charge.

2. The weight of sinter per 1,000 kg. of dry charge, and its proximate analysis.

3. The volume of air theoretically required for the roasting of 1,000 kg. of dry charge. (One atom of S from the FeS_2 is expelled without oxidation, balance of the S goes to SO_2.)

4. The percentage composition of the gases in the suction box (CO_2, H_2O, SO_2, N_2, O_2).

5. The percentage of air drawn in, in excess of the theoretical requirement.

239. The suspension, or flash, roasting furnaces of the Consolidated Mining & Smelting Co. at Trail, B.C., receive a charge of zinc concentrates containing 51.1 per cent Zn, 3.5 Pb, 12.2 Fe, 32.8 S, balance SiO_2 and CaO. (Dry analysis; for simplification, 0.8 per cent Mn + Cu + Cd has been included with the Fe.) The concentrates also contain H_2O equal to 9.5 per cent of the dry weight. The roasted product carries 0.6 per cent sulphide sulphur (assume contained in ZnS) and 1.7 per cent sulphate sulphur (assume contained in $ZnSO_4$). The rest of the zinc forms ZnO, Pb forms PbO, and Fe forms Fe_2O_3. No fuel is used.

The gases (wet) leaving the furnace contain 9.0 per cent SO_2. They go to waste-heat boilers, entering the boiler at 1500°F. The boilers generate 200 boiler hp. for each 100 tons of concentrates (wet) roasted per day.

Required. 1. The weight of roasted ore, per 100 tons of wet concentrates.

2. The theoretical volume of air required for the roasting reactions, per 100 tons of concentrates.

3. The volume of the gases leaving the furnace, referred to standard conditions (wet).

4. The percentage of excess air used.

5. The efficiency of the boilers (disregarding heat content of dust carried into boilers).

240. Zinc concentrates from the Joplin district are composed of 60 per cent zinc, present as ZnS, iron present as FeS, and 7 per cent SiO_2.

These are roasted, zinc being oxidized to ZnO, iron to Fe_2O_3, and sulphur to SO_2. 3 per cent of the ZnS, however, remains unchanged.

Coal equal to 20 per cent of the raw ore is used; the ashes from the coal do not mix with the ore, but the products of combustion pass through the furnace and into the flue mixed with the gases from the roasting. The coal is 72 per cent C, 6 H, 8 O, 2 S, 12 ash.

The flue gases carry 12 per cent oxygen.

Required: 1. The weight of roasted ore, per metric ton of raw ore; and the percentage of sulphur in the roasted ore.

2. The theoretical volume of air used for roasting and for combustion of the coal, per ton of raw ore.

3. The percentage composition of the flue gases and the percentage excess air used above the theoretical requirement for roasting and combustion.

4. The percentages of the total heat that are supplied by the combustion of the fuel and by the roasting reactions.

241. Flotation concentrates were roasted at Palmerton, Pa., in a Mathiessen-Hegeler furnace which received 1,400 kg. of concentrates (wet) every 45 min. The concentrates contained 57 per cent Zn and 32 per cent S (dry analysis) and in addition H_2O equal to 12 per cent of the dry material. Assume that the sulphur not present as ZnS was present as FeS_2, and the balance of the ore was SiO_2. The roasted ore carried 1 per cent S.

The gases left the furnace at 340°C. The roasted ore was discharged at 400°C.

The gases contained 4.75 per cent SO_2 and were used to make sulphuric acid.

Heat was supplied to the lower hearths by burning 25 cu. m. of producer gas per minute, having a calorific power of 1,300 Cal. per cubic meter. Assume that the gas supplied this heat to the muffles at a thermal efficiency of 10 per cent. The products of combustion did not mix with the roaster gases.

Required: 1. The tons of roasted ore produced in 24 hr.

2. The kilograms of H_2SO_4 made, assuming 100 per cent conversion, in 24 hr

3. The amount of air admitted to the muffles, expressed as percentage excess over the theoretical requirement for oxidation.

4. A heat balance of the furnace, per 1,400 kg. of concentrates charged.

CHAPTER XV

COPPER SMELTING AND CONVERTING

Copper ores are usually smelted to matte, which for purposes of calculation is usually taken as a simple molten solution of Cu_2S and FeS. The percentage of copper in the matte—commonly termed the "grade" of the matte—thus determines the percentage composition in Cu, Fe, and S of this ideal matte; the percentage of Cu multiplied by $^{160}/_{128}$ gives the percentage of Cu_2S, and the balance is FeS.

Actually, matte will contain minor amounts of other sulphides as impurities—PbS and ZnS in particular—and also important amounts of Fe_3O_4, sometimes accompanied by metallic Fe. In practice it may often be best to take account of iron in these forms in making computations both in smelting and in converting; but ordinarily it is customary to consider all the iron present in matte as FeS, and this assumption will be made here in order to simplify the general discussion and the introductory problems.

High-grade mattes commonly have part of their copper content present as free Cu.

Matte also contains the precious metals; but, though very important in value, in percentage the amounts of these are too small to affect the calculation. In the problems dealing with precious metals, value will figure prominently.

Although costs and values are not considered in most of the problems in this book, for the reason that such calculations involve for the most part arithmetic of an entirely obvious character, the student must not lose sight of the fact that in practice these items are primary considerations—in the last analysis the determining factors in the adoption of methods of operation Doubtless, most plant managers do more figuring in dollars and cents than in pounds and calories. The work with pounds and calories, however, is the part involving those technical principles which require study as an essential part of the metallurgist's training.

The action in a copper smelting furnace and also in a converter is governed by the fact that sulphur has a greater affinity for copper than for iron. (Though the heat of formation of FeS is greater than that of Cu_2S, the oxidation of FeS has greater free energy change than the oxidation of Cu_2S, and the reaction $2CuO + FeS = Cu_2S + FeO$ will take place from left to right as shown.) The grade of matte formed in smelting depends directly on the amount of sulphur charged. The copper in the charge takes enough sulphur to form Cu_2S, and the rest of the sulphur not oxidized forms FeS; therefore, the more sulphur available, the more FeS is formed and the lower the percentage of copper in the resulting matte. The sulphur charged is divided between the matte and the gases, the latter part mostly burning to SO_2. Although the copper reverberatory is essentially a melting furnace and although an effort is made to ensure melting of the charge as soon as possible after it enters the furnace, there is always some oxidation with consequent elimination of sulphur. The amount oxidized varies, depending upon the character of the charge, the method of charging, design of the furnace, and various other factors. The furnace operator can learn this important quantity for his own operation from a study of the charge and products. Usually between 15 and 30 per cent of the sulphur charged is eliminated as SO_2. In the copper blast furnace, which is now used in only a few places, the percentage is greater.

The iron charged is divided between the matte and the slag. The iron not entering the matte forms FeO, a principal component of the slag.

The copper may in most problems be assumed to go entirely into the matte. The loss of copper in the slag, while extremely important, is too small to be considered in most types of calculation; it is usually less than 0.5 per cent of the slag.

The problem of calculating the products from a given charge in copper smelting will be illustrated, and then the more difficult question of calculating the charge to yield a desired matte and slag will be taken up.

Example 27

A blast furnace smelts a mixture of ores having the following components:

	Per Cent		Per Cent
Chalcopyrite ($CuFeS_2$)	12	Iron oxide (Fe_2O_3)	18
Pyrite (FeS_2)	34	Silica (SiO_2)	23
Enargite (Cu_3AsS_4)	7	Lime (CaO)	3
Melaconite (CuO)	3		

The weight of the mixture charged per day is 600 tons of 2,000 lb In addition, $CaCO_3$ is added as flux, sufficient to yield a slag of 20 per cent CaO.

Assume that all the arsenic enters the gases as As_2O_3. The gases contain no CO or free oxygen.

Coke is used amounting to 8 per cent of the ore mixture. Its composition is 85 per cent C and 15 per cent SiO_2.

The matte carries 40 per cent copper.

Required: 1. The weight of matte produced, per day

2. The weight of the slag, per ton of ore.
3. The weight of $CaCO_3$ used, per ton of ore.
4. The volume of the blast, per ton of ore.
5. The volume and composition of the gases, per ton of ore.
6. The weight of As_2O_3 in the gases, per day.

Solution. The total weight of copper charged per ton of ore, as determined from the compounds and percentages given, is 199.4 lb. The weight of the matte is therefore $\frac{199.4}{0.40} = 498.5$ lb. per ton of ore = 149.5 tons per day (1).

40 per cent Cu × $^{160}/_{128}$ = 50 per cent Cu_2S in the matte. The matte is therefore 50 per cent FeS = 31.8 per cent Fe.

0.318 × 498.5 = 158.5 lb. of Fe in the matte. The total weight of Fe as calculated from the charge is 642 lb. 642 − 158.5 = 483.5 lb. of Fe in the slag

$$483.5 \times {}^{72}/_{56} = 621 \text{ lb. FeO.}$$
$$0.23 \times 2{,}000 = 460 \text{ lb. } SiO_2.$$

There is also SiO_2 in the coke, amounting to 0.15 × 0.08 × 2,000 = 24 lb. The sum of the FeO and SiO_2, or 1,105 lb., constitutes 80 per cent of the weight of the slag. $\frac{1{,}105}{0.80} = 1{,}381$ lb. slag (2).

1,381 − 1,105 = 276 lb. of CaO in the slag, of which 60 lb. is in the ore. 276 − 60 = 216 lb. supplied by $CaCO_3$ $^{100}/_{56}$ × 216 = 386 lb. of $CaCO_3$ used (3).

The percentage of sulphur in the matte is (50 − 40) + (50 − 31.8) = 28.2 per cent 0.282 × 498.5 = 140.5 lb. The total weight of sulphur charged is 310 lb. 310 − 140.5 = 169.5 lb. of sulphur goes into the gases

O required for SO_2 = $^{32}/_{32}$ × 169.5 = 169.5 lb
O for FeO = 621 − 483.5 = 137.5
O for As_2O_3 = $^{48}{}_{150}$ × $^{75}/_{395}$ × 140 = 8.6
O for coke = $^{32}/_{12}$ × 0.85 × 160 = 382.6
Total O required = 698.2 lb., part of which is derived from the charge and part from the blast

O derived from the charge:

From Fe_2O_3 = $^{48}{}_{160}$ × 360 = 108 lb.
CuO = $^{16}{}_{80}$ × 60 = 12
120 lb.

O from blast = 698.2 − 120 = 578.2 lb

578.2 × $^{359}/_{32}$ = 6,490 cu. ft. of O_2 = 30,900 cu. ft. of blast per ton of ore (4)
CO_2 from $CaCO_3$ = 375 − 210 = 165 lb
CO_2 from coke = $^{44}/_{32}$ × 382.6 = 526 lb
Volume of CO_2 = 691 × $^{359}/_{44}$ = 5,640 cu. ft = 17.6 per cent
SO_2 = 169.5 × $^{359}/_{32}$ = 1,900 = 5.9
As_2O_3 = 8.6 × $^{359}/_{48}$ = 60 = 0.2
N_2 = 30,900 − 6,490 = 24,410 = 76.3
32,010 cu. ft. = 100.0 per cent (5).

8.6 × $^{198}/_{48}$ × 600 = 21,300 lb. of As_2O_3 per day (6).

Charge Calculation for Copper Smelting.—A charge calculation for a copper reverberatory will now be carried out, using the common arithmetical, or "available-flux," method. Other methods of charge calculation have been discussed in connection with the iron blast furnace (Chap. X) and can be applied to this problem if desired.

The method begins with taking 100 parts (either pounds or kilograms) of roasted ore—the ore which will be the largest constituent of the charge—and then determining how many parts of each of the other constituents must be used with this amount of roasted ore to produce the desired matte and slag. The roasted ore will contain insufficient sulphur to form the proper matte, and the first determination is the amount of raw (sulphurrich) ore needed to supply the sulphur deficiency in 100 parts of roasted ore. Since the raw ore contains copper, it must have some sulphur to satisfy the requirements of its own copper, and only the excess over this amount is available for supplying the deficiency in the roasted ore.

The amount of raw ore to make the desired matte having been found, the amounts of SiO_2 and FeO which the two ores will supply to the slag are next determined. Usually it will be found that there is not enough FeO to satisfy the SiO_2:FeO ratio required for the slag. Consequently an iron-ore flux must be used, and the amount necessary for the ores already taken is now calculated, it being still borne in mind that the iron-ore flux itself contains SiO_2 and only a certain excess of FeO is available for slagging the SiO_2 of other constituents. In the case of a blast furnace, or of a reverberatory using pulverized coal, silica in the ash would also have to be fluxed. Finally the amount of limestone necessary to make the desired slag ratio is found.

Example 28

The following materials are available for smelting in a reverberatory furnace:

A. Roasted ore, per cent	*B.* Raw ore, per cent	*C.* Iron-ore flux, per cent	*D.* Limestone, per cent
Cu_2S 14	$CuFeS_2$ 30	Fe_2O_3 80	$CaCO_3$ 80
FeS 10	FeS_2 20	SiO_2 12	$MgCO_3$ 15
Fe_2O_3 31	SiO_2 50	Al_2O_3 3	Fe_2O_3 3
SiO_2 36		$CaCO_3$ 5	SiO_2 2
Al_2O_3 9			

The furnace is fired with powdered coal and will require 13 parts of coal per 100 parts of charge. The coal carries 15 per cent ash, the ash being 90 per cent SiO_2 and 10 per cent FeO. Assume that one-half the ash falls on the charge, the remainder being carried out in suspension in the gases.

Assume that 20 per cent of the sulphur charged goes into the gases. Disregard loss of flue dust and copper loss in the slag.

Required: Make up a charge of 1,000 lb. total to yield a 42 per cent matte and a slag having the ratio SiO_2:CaO:FeO = 40:15:45, counting MgO as CaO in equivalent proportions (*i.e.*, 24 MgO = 40 CaO).

Solution: The ratio of Cu:Fe:S which must be maintained for a matte of 42 per cent Cu is first to be established.

42 Cu × $^{160}/_{128}$ = 52.5 Cu_2S, containing 10.5 S.

100 − 52.5 = 47.5 FeS, containing 17.3 S.

The established ratio is therefore Cu:Fe:S = 42:30.2:27.8.

Take 100 lb. of *A*. Cu in it = $^{128}/_{160}$ × 14 = 11.2. S required by Cu and Fe according to the matte ratio = $\frac{27.8}{42}$ × 11.2 = 7.41. S present (taking only four-fifths because one-fifth is lost to the gases) = $^{4}/_{5}$($^{32}/_{160}$ × 14 + $^{32}/_{88}$ × 10) = 5.15. Deficit of S = 7.41 − 5.15 = 2.26.

How much S is available in 1 part of *B* to supply this deficit? Total S in *B* = $^{64}/_{184}$ × 0.30 + $^{64}/_{120}$ × 0.20 = 0.211. $^{4}/_{5}$ × 0.211 = 0.169. Cu in *B* = $^{64}/_{184}$ × 0.30 = 0.1043.

S required by this Cu = $\frac{27.8}{42}$ × 0.1043 = 0.069

Excess S in *B* available to supply deficit in *A* = 0.169 − 0.069 = 0.100.

Pounds of *B* to go with 100 lb of *A* therefore = $\frac{2.26}{0.100}$ = 22.6

How much FeO and SiO_2 are now in the slag? From the total Fe present, deduct the Fe in the matte:

$$\begin{array}{lr} \text{Fe in 100 lb of } A = \,^{56}/_{88} \times 10 + \,^{112}/_{160} \times 31 & = 28.1 \\ \text{Fe in 22.6 lb. of } B = \,^{56}/_{184} \times 0.30 \times 22.6 + \,^{56}/_{120} \times 0.20 \times 22.6 & = \underline{4.4} \\ \text{Total Fe charged} & = 32.5 \end{array}$$

Cu charged = 11.2 + 0.1043 × 22.6 = 13.56. Fe in matte according to established ratio = $\frac{30.2}{42}$ × 13.56 = 9.8

Fe to slag = 32.5 − 9.8 = 22.7. FeO = $^{72}/_{56}$ × 22.7 = 29.2. SiO_2 in 100 lb of *A* and 22.6 lb. of *B* = 36 + 11.3 = 47.3. FeO required by this SiO_2 according to desired slag ratio = $^{45}/_{40}$ × 47.3 = 53.2. Deficit of FeO = 53.2 − 29.2 = 24.0 lb

How much available FeO in 1 part of *C*? FeO in *C* = $^{144}/_{160}$ × 0.80 = 0.72. FeO needed by *C* for its own SiO_2 = $^{45}/_{40}$ × 0.12 = 0.135. Available FeO = 0.72 − 0.135 = 0.585

$\frac{24.0}{0.585}$ = 41.0 lb of *C* needed.

Total SiO_2 now used = 47.3 + 0.12 × 41 = 52.2 lb. CaO needed to go with this = $^{15}/_{40}$ × 52.2 = 19.6 lb. CaO in 41 lb. of *C* = $^{56}/_{100}$ × 0.05 × 41 = 1.1. CaO to be supplied = 19.6 − 1.1 = 18.5 lb

How much available CaO in 1 part of *D*? CaO in *D* = $^{56}/_{100}$ × 0.80 + $^{56}/_{40}$ × $^{40}/_{84}$ × 0.15 = 54.8. CaO needed by *D* for its own SiO_2 = $^{15}/_{40}$ × 0.02 = 0.008. CaO available = 0.548 − 0.008 = 0.540.

$\frac{18.5}{0.54}$ = 34.3 lb. of *D* needed.

The additional SiO_2 added in *D* should have FeO as well as CaO with it. However, *D* contains some FeO, evidently in somewhere near the right amount; and since the amount is very small, the slag ratio is not appreciably disturbed

It is now necessary to provide FeO and CaO for the SiO_2 of the coal ash.

Weight of coal used = 0.13(100 + 22.6 + 41 + 34.3) = 25.7 lb. Ash to charge = $^{1}/_{2}$ × 0.15 × 25.7 = 1.93. SiO_2 in this = 0.90 × 1.93 = 1.74. FeO needed = $^{45}/_{40}$ × 1.74 = 1.96. FeO present = 0.10 × 1.93 = 0.19. FeO to be added = 1.96 − 0.19 = 1.77.

$\frac{1.77}{0.585}$ = 3.0 lb. of additional *C* needed.

CaO needed = $^{15}\!/_{40} \times 1.74 = 0.65$. CaO added in the additional $C = {}^{56}\!/_{100} \times 0.05 \times 3.0 = 0.08$. CaO to be added $= 0.65 - 0.08 = 0.57$.

$\frac{0.57}{0.54} = 1.1$ lb. of additional D needed.

Total charge:

$$\begin{array}{llll}
A = 100.0 \text{ lb.} & \frac{1,000}{202} \times 100 & = & 495 \text{ lb. roasted ore} \\
B = 22.6 & \frac{1,000}{202} \times 22.6 & = & 112 \text{ lb. raw ore} \\
C = 44.0 & \frac{1,000}{202} \times 44 & = & 218 \text{ lb. iron-ore flux} \\
D = 35.4 & \frac{1,000}{202} \times 35.4 & = & 175 \text{ lb. limestone} \\
\overline{202.0 \text{ lb.}} & & & \overline{1,000 \text{ lb}} \text{ charge}
\end{array}$$

Thermochemical Constants in Copper Smelting.—Data needed for calculation of heat balances in copper smelting and converting are in many cases uncertain or entirely lacking. Data applied to copper mattes are for the most part based on constants for Cu_2S and FeS, but it should be remembered that in practice copper mattes depart widely from the state of being solutions merely of these two compounds. Some constants which may be used in the absence of more precise values are recommended in the following paragraphs.

For the heat of formation of copper matte, accurate values are available (see Table XLVII, p. 420) for the formation of Cu_2S and FeS, but not for the solution of one of these compounds in the other. This heat of solution is known to be small and has usually been taken as zero. However, some work on the heat of formation of $CuFeS_2$ indicates the following as approximate values for the heat of solution of Cu_2S with FeS: For matte up to 36 per cent Cu, 16 Cal. liberated per kilogram of Cu_2S, falling thereafter 1 Cal. for each rise of 2 per cent Cu, resulting in a value of 10 Cal. per kilogram of Cu_2S in a 48 per cent (Cu) matte and of 4 Cal for a 60 per cent matte

The heat of formation of $CuFeS_2$ from the elements is 40,130 Cal. liberated per mol of $CuFeS_2$, and its heat of formation from the compounds Cu_2S, FeS, and FeS_2 is 1,327 Cal. liberated per mol of $CuFeS_2$ ($2CuFeS_2 = Cu_2S + FeS + FeS_2 = Cu_2S + 2FeS + S$.)

The melting point of Cu_2S is 1127°C., and its heat of fusion is 34.5 Cal. per kilogram. The melting point of FeS is 1195°C., and its heat of fusion 57 Cal. per kilogram. Carpenter and Hayward determined that Cu_2S and FeS form a eutectic containing 32 per cent Cu_2S and melting at 995°C. The heat of fusion will fall as the melting point falls; for a matte containing 47.3 per cent Cu (= 58.2 Cu_2S) it has been determined as 30.1 Cal. At the eutectic (32 per cent Cu_2S) the heat of fusion would be about 28.

Specific heats of solid Cu_2S and FeS are given in Table XIX. The specific heat of liquid matte is usually taken as 0.14, and the heat content of liquid matte at the melting point of 1000°C. as about 200 Cal. per kilogram.

The mean specific heat of a slag containing 36 SiO_2:40 FeO:11 CaO between 0 and 1100°C. was determined as $0.202 + 0.000015t$. The heat of fusion of a slag melting at 1114°C. was 38.6 Cal. per kilogram. These figures indicate a heat content of the liquid slag at 1114°C. of 282 Cal. per kilogram. However, the heat content of a slag melting at 1100°C. is usually taken as about 300 Cal. per kilogram with an increase of 10 Cal. for each rise of 20° above 1100°C. The specific heat of liquid reverberatory slag is usually taken as 0.28 and that of liquid converter slag as 0.25.

Converting.—The operation of the copper converter is divided into two stages. The first, or slag-forming, stage consists in the oxidation of FeS to FeO and accompanying combination of the FeO with SiO_2 added as flux:

$$2FeS + 3O_2 = 2FeO + 2SO_2.$$
$$xFeO + ySiO_2 = xFeO.ySiO_2.$$

At the end of the first stage the slag is poured off; the material remaining consists mostly (theoretically entirely) of Cu_2S, called "white metal." The second stage is the oxidation of Cu_2S to blister copper:

$$Cu_2S + O_2 = 2Cu + SO_2.$$

Theoretically no slag is made during the second stage, and this may be assumed to be the case in calculations. There is some oxidation of copper to CuO, most of which would doubtless be reduced again, so long as sulphide remained with which it could react, but for the fact that some of it is taken up by the silica to form a silicate which enters the slag. The slag contains so much copper (usually 3 or 4 per cent) that in many calculations this factor should not be ignored, though often it may be. It is usually permissible to assume that copper is in the slag as CuO, although undoubtedly some of it is Cu_2S.

As previously noted, the matte normally contains Fe_3O_4 and often Fe, but it is usual to count all the iron as FeS. The slag is usually assumed to have its iron content entirely as FeO, though actually its percentage of Fe_3O_4 is often nearly as large as the FeO. When complete analyses of matte and slag are available, it is well to take these facts into account; but for illustration of the principles involved they may be disregarded.

After the first charge of matte has been blown to white metal and the slag poured, the converter is usually filled with matte again before blowing down to blister copper. This refilling may be repeated several times with large converters.

The flux may be added in batches or continuously, the latter method now being the usual one. If it is added in batches in a small converter, enough may be added at or near the beginning of the blow to flux all the iron oxide that will be formed from the matte. But in a converter of large matte capacity it would not be possible to add so much cold flux at once. A method that has sometimes been used in such cases is addition in several small batches and blowing and pouring the slag when sufficient iron has been oxidized to form a proper slag with the amount of flux added. Thus the first stage would be divided into several "partial blows." This method, however, has given way in favor of continuous automatic charging of flux. Flux, which is usually a clean siliceous copper ore, is dried before charging and may be warm when it enters the converter.

The amount of flux added is proportioned according to the desired slag composition. This is usually about 3 parts SiO_2 to 7 parts FeO. No fuel is used, and the blast is not preheated. There is no free oxygen in the gases.

In order to keep the converter from becoming too hot during blowing, the blow is interrupted and some cold material added. This is often scrap copper and in many calculations need not be considered. In other cases these additions may be very important factors.

Example 29

In the operation of a copper converter, the first charge is 30 tons of 42 per cent matte. The flux used is ore carrying Cu, 7 per cent; Fe, 16; S, 5, SiO_2, 49. The slag carries 28 per cent SiO_2, 63 FeO; 4 CuO. After the first slag is poured, additional matte is charged of the same weight as the FeS which has been oxidized from the first matte charge. The time of the blister-forming stage is 2 hr

Required: 1. The total weight of flux used, and the total weight of slag made.
2. The weight of blister copper formed, taking it as pure Cu.
3. The cubic meters of blast used.
4. The total blowing time, and the volume of blast supplied, per minute.

Solution:

$30{,}000 \times 0.42 = 12{,}600$ kg. Cu $\times\ {}^{5}\!/_{4} = 15{,}750$ kg Cu_2S.
$30{,}000 - 15{,}750 = 14{,}250$ kg. FeS.
Second matte: $14{,}250 \times 0.42 = 5{,}985$ Cu $\times\ {}^{5}\!/_{4} = 7{,}480$ kg. Cu_2S.
$14{,}250 - 7{,}480 = 6{,}770$ kg. FeS.
$14{,}250 + 6{,}770 = 21{,}020$ FeS $\times\ {}^{72}\!/_{88} = 17{,}190$ FeO.

Available SiO_2 in flux:

Cu $= 0.07 \times {}^{5}\!/_{4} = 0.0875$ Cu_2S. FeO $= 0.16 \times {}^{72}\!/_{56} = 0.206$.
SiO_2 for FeO $= {}^{28}\!/_{63} \times 0.206 = 0.092$.
SiO_2 available $= 0.49 - 0.092 = 0.398$
SiO_2 required for FeO in matte $= {}^{28}\!/_{63} \times 17{,}190 = 7{,}640$ kg.

$$\text{Flux used} = \frac{7{,}640}{0.398} = 19{,}200 \text{ kg. (1).}$$

$$\text{Slag made} = \frac{0.49 \times 19{,}200}{0.28} = 33{,}600 \text{ kg. (1).}$$

$$\begin{aligned}
\text{Cu in matte} &= 12{,}600 + 5{,}990 = 18{,}590 \text{ kg.}\\
\text{Cu in flux} &= 0.07 \times 19{,}200 = \underline{1{,}340}\\
&\qquad 19{,}930 \text{ kg.}\\
\text{Cu in slag} &= 0.04 \times 33{,}600 \times \frac{64}{80} = \underline{1{,}070}\\
&\qquad 18{,}860 \text{ kg. of blister Cu (2).}
\end{aligned}$$

S in flux $= 0.05$. S with Fe in flux $= 0.05 - 0.0175 = 0.0325$.
FeS $= 0.0325 \times {}^{88}\!/_{32} = 0.0894 \times 19{,}200 = 1{,}710$ kg.

Total FeS oxidized = 14,250 + 6,770 + 1,710 = 22,730 kg.

$$2FeS + 3O_2 = 2FeO + 2SO_2.$$

$$O_2 \text{ required} = \frac{3 \times 22.4}{176} \times 22{,}730 = 8{,}680 \text{ cu. m.}$$

$$Cu_2S + 2O_2 = 2CuO + SO_2$$

$$O_2 \text{ required} = \frac{2 \times 22.4}{128} \times 1{,}070 = \underline{380}$$

$$\text{Total } O_2 \text{ in slag-forming stage} = 9{,}060 \text{ cu. m.}$$

$$Cu_2S + O_2 = 2Cu + SO_2$$

$$O_2 \text{ in blister-forming stage} = \frac{22.4}{128} \times 18{,}860 = 3{,}300 \text{ cu. m.}$$

$$9{,}060 + 3{,}300 = 12{,}360 \text{ cu. m. } O_2.$$

$$\frac{12{,}360}{0.21} = 58{,}900 \text{ cu. m. blast (3)}$$

$$\frac{12{,}360}{3{,}300} \times 2.0 = 7.5 \text{ hr. total blowing time.}$$

$$\frac{58{,}900}{7.5 \times 60} = 131 \text{ cu. m. per minute (4).}$$

Temperature Rise in the Converter.—The heat balance of a converter is interesting because no fuel is used and because of the careful control of temperature needed to keep the converter from getting so hot as to damage the lining seriously. The maximum permissible temperature may be about 1300°C. or less. Instead of the usual form of heat balance, an example will be given illustrating the possibility of using a thermal-balance calculation to form an idea of the rate of temperature rise in the converter or the maximum possible rate of blowing without exceeding a given temperature. It is necessary first to obtain the approximate loss of heat by radiation and conduction. This may be done by allowing the converter to stand with a charge of matte, but without blowing, and measuring the fall in temperature at the end of a certain period, say 20 min. The heat balance is best taken on the basis of the charge in the converter, exclusive of the converter itself. High accuracy should not be expected from the results of this calculation, as too many assumptions are necessary; but it is, nevertheless, instructive.

Example 30

The matte is charged into the converter of the preceding example at a temperature of 1050°C. The flux is at 60° and the blast at 30°. It is found by experiment that if the converter is allowed to stand without blowing after the matte is first poured in the matte will cool at the rate of 6° per minute.

Assume that the heat lost by conduction through the walls of the converter is proportional to the temperature of the matte. Assume that the matte, the slag, and the gases leaving the converter are all at the same temperature.

The melting point of the matte is 1000°C., and its specific heat (liquid) is 0.14. Assume these to be the same for all compositions. The heat content of the matte at its melting point is 205 Cal. per kilogram.

Assume that the heat of formation of the slag is approximately that of the compound $2FeO.SiO_2$ (the compound approximates the $FeO.SiO_2$ ratio of 70:30). The heat content of the molten slag at its melting point, 1120°C., is 300 Cal. per kilogram. The specific heat of the molten slag is 0.27.

Required: 1. If no material other than the flux were added to the converter matte charge, how fast should the charge be blown to just reach the temperature of 1150° at the end of the first slag-forming period? State result in minimum time for the blow and the number of cubic meters of air supplied per minute

2. If, during the blow, 5 tons of scrap copper were added, the blow being halted for 10 min. at the average temperature of 1100° in order to add this material, how fast could the charge be blown?

Solution: The rate at which the converter can be blown depends on the relative rates of generation and loss of heat. The net heat left in the converter charge (heat generated and supplied minus heat lost) per minute determines the number of minutes required for the temperature to rise from 1050 to 1150°. The calculation will be based on finding the total heat available and subtracting the total heat contained in the products (white metal, slag, and gases), leaving the heat which must be dispersed by radiation and conduction. Since the *rate* at which this dispersion goes on is approximately known, the time required may be calculated from it.

Heat content of matte at the start (1050°) = $30{,}000(205 + 50 \times 0.14) = 6{,}360{,}000$ Cal.

From the previous example it is seen that the first slag-forming period is $\frac{30{,}000}{44{,}250}$, or 67.8 per cent of the whole slag-forming stage. The volume of blast in the first period is therefore $0.678 \times \frac{9{,}060}{0.21} = 29{,}200$ cu. m.

Heat entering in the blast $= 29{,}200(0.302 + 0.000022 \times 30)30 = 265{,}000$ Cal.

Since the temperature of the flux is only 60°, its heat content will be small and it will be permissible to regard it as pure SiO_2 in calculating the heat content

Heat entering in the flux $= 0.678 \times 19{,}200(0.1833 + 0.000077 \times 60)60 =$ 147,000 Cal.

Heat generated: The heat of the main reaction is:

$$2FeS + 3O_2 = 2FeO + 2SO_2$$
$$2(23{,}100) - 2(64{,}300) - 2(70{,}940); \qquad \Delta H = -224{,}280 \text{ Cal.}$$

The total FeS oxidized includes the FeS in the flux. Assume that the S in the flux not combined as Cu_2S exists as FeS. $5 - \frac{32}{128} \times 7 = 3.25$ per cent. The per cent FeS then is $\frac{88}{32} \times 3.25 = 8.9$, and the weight of FeS $= 0.089 \times 0.678 \times 19{,}200 = 1{,}160$ kg. Total FeS oxidized $= 14{,}250 + 1{,}160 = 15{,}410$ kg.

Heat generated $= 15{,}410 \times \frac{224{,}280}{176} = 19{,}650{,}000$ Cal

Heat is also generated by oxidation of some Cu_2S to CuO:

$$Cu_2S + 2O_2 = 2CuO + SO_2$$
$$18{,}950 - 2(38{,}500) - 70{,}940; \qquad \Delta H = -128{,}990 \text{ Cal.}$$

Cu oxidized in this period $= 0.678 \times 1{,}070 = 725$ kg.

Heat generated $= 725 \times \frac{128{,}990}{128} = 730{,}000$ Cal.

Heat of slag formation, 153 Cal. per kilogram of FeO:

$$0.63 \times (0.678 \times 33{,}600) \times 153 = 2{,}196{,}000 \text{ Cal. generated.}$$

Total heat available $= 6{,}630{,}000 + 265{,}000 + 147{,}000 + 19{,}650{,}000 + 730{,}000 + 2{,}196{,}000 = 29{,}618{,}000$ Cal.

Weight of matte (Cu_2S) at the end $= 0.678 \times 18{,}860 \times {}^{160}/_{128} = 16{,}000$ kg.

Heat contained in this at 1150° $= 16{,}000(205 + 150 \times 0.14) = 3{,}616{,}000$ Cal.

Heat in the slag: $0.678 \times 33{,}600(300 + 30 \times 0.27) = 7{,}020{,}000$ Cal.

Heat in the gases: $N_2 = 0.79 \times 29{,}200 = 23{,}100$ cu. m.

$$SO_2 = 0.678(\tfrac{2}{3} \times 8{,}680 + 380) = 4{,}180 \text{ cu. m.}$$

The average temperature of the gases is the mean between 1050 and 1150°

$$\begin{aligned} \text{Heat in } N_2 &= 23{,}100(0.302 + 0.000022 \times 1{,}100)1{,}100 = 8{,}280{,}000 \text{ Cal.} \\ SO_2 &= 4{,}180(0.406 + 0.00009 \times 1{,}100)1{,}100 = \underline{2{,}340{,}000} \\ &\qquad\qquad\qquad\qquad\qquad\qquad\qquad 10{,}620{,}000 \text{ Cal} \end{aligned}$$

Total heat accounted for $= 3{,}616{,}000 + 7{,}020{,}000 + 10{,}620{,}000 = 21{,}256{,}000$ Cal.

Total heat lost by radiation, etc., $= 29{,}618{,}000 - 21{,}256{,}000 = 8{,}362{,}000$ Cal

Heat lost by radiation, etc., in 1 min. $= \dfrac{1{,}100}{1{,}050} \times 6 \times 30{,}000 \times 0.14 = 26{,}400$ Cal.

Time to disperse 8,362,000 Cal. $= \dfrac{8{,}362{,}000}{26{,}400} = 317$ min.

Therefore, the minimum blowing time is 317 min = 5 hr. 17 min.

The maximum blowing rate is $\dfrac{29{,}200}{317} = 92$ cu. m. per minute (1).

If 5,000 kg. of Cu is added during this stage, it will form Cu_2S according to the reaction $FeS + 2Cu = Cu_2S + Fe$, the Fe at the same time being oxidized to FeO. This differs from the former reaction, $FeS + {}^3/_2O_2 = FeO + SO_2$, in that Cu_2S is formed and SO_2 is not formed. The loss of heat, therefore, is the difference between the heats of formation of SO_2 and Cu_2S. In addition, heat is taken up and held by the Cu_2S formed. However, less air is needed because SO_2 is not formed and less nitrogen passes out of the converter. The heat corresponding to these modifications will now be calculated and deducted from the loss by radiation, etc., found above. There is also some loss of heat during the 10 min. that the converter is standing.

Weight of S taken up by 5,000 Cu $= {}^{32}/_{128} \times 5{,}000 = 1{,}250$ kg.

$1{,}250 \times 2{,}212 = 2{,}765{,}000$ Cal. for $S \rightarrow SO_2$

$5{,}000 \times 149 = \underline{745{,}000}$ Cal. for $Cu \rightarrow Cu_2S$

$2{,}020{,}000$ Cal. saved

Additional heat taken up by $Cu_2S = 6{,}250 \times 226 = 1{,}412{,}000$ Cal.

Heat lost in 10 min. standing $= 10 \times 26{,}400 = 264{,}000$ Cal.

$$\text{Volume of } SO_2 \text{ saved} = 1{,}250 \times \frac{22.4}{32} = 874 \text{ cu. m.}$$

$$\text{Volume of } N_2 \text{ saved} = 874 \times {}^{79}/_{21} = 3{,}270 \text{ cu. m.}$$

Heat contained in SO_2 and $N_2 = \dfrac{874}{4{,}180} \times 2{,}340{,}000 + \dfrac{3{,}270}{23{,}100} \times 8{,}280{,}000 =$ 1,660,000 Cal.

(The heat loss due to the smaller amount of blast entering at 30° is negligible.)

Total heat to be deducted from heat available $= 2{,}020{,}000 + 264{,}000 = 2{,}284{,}000$ Cal. $29{,}618{,}000 - 2{,}284{,}000 = 27{,}334{,}000$ Cal. available.

Total heat to be added to heat accounted for $= 1{,}412{,}000 - 1{,}660{,}000 = -248{,}000$ Cal. $21{,}256{,}000 - 248{,}000 = 21{,}008{,}000$ Cal.

Heat loss by radiation, etc., $= 27{,}334{,}000 - 21{,}008{,}000 = 6{,}326{,}000$ Cal.

$$\frac{6{,}326{,}000}{26{,}400} = 240 \text{ min.} = 4.0 \text{ hr.}$$

The blast required is 4,144 cu. m. less than before.

$$\frac{29{,}200 - 4{,}144}{240} = 104 \text{ cu. m. per minute (2).}$$

This result indicates that the rate of blowing, as measured by the volume of blast per minute, may be increased 14 per cent if 5 tons of scrap copper is added to cool the converter.

Problems

242. 1. A copper ore carries 30 per cent chalcopyrite ($CuFeS_2$), 20 pyrite (FeS_2), 50 SiO_2. What percentages of Cu, Fe, and S does it contain?

2. What would be the percentage of gangue in a cuprite (Cu_2O) ore having the same copper content as in 1?

3. A copper matte may be expressed by the formula $xCu_2S\ yFeS$, with no fixed values for x and y. What would be the entire percentage composition of a matte containing 38 per cent Cu?

4. If the ore in 1 is fused down and only the excess sulphur eliminated, what would be the composition of the resulting matte?

5. What percentage of the iron content of the ore in 1 would have to be eliminated in order to make a 38 per cent matte?

6. Assuming the oxygen of the cuprite in 2 to combine with the excess sulphur from the other ore, in what proportions should the two ores be mixed to make a matte, with no leftovers and no oxidation of Fe, and what would be the composition of the matte?

243. A copper ore carries the following:

	Per Cent
Cu_2S	18
FeS_2	55
SiO_2	27

It is smelted in a reverberatory furnace, using pure $CaCO_3$ as flux. The slag is to contain 35 per cent FeO and 20 per cent CaO.

Required: Per ton of ore:

1. The weight of limestone needed
2. The weight of slag made.
3. The weight of matte.
4. The volume of air theoretically required by the charge

244. A copper ore contains the following:

	Per Cent		Per Cent
$CuFeS_2$	21.2	FeS_2	15.7
Cu_2S	3.6	Fe_3O_4	4.6
$Cu_4Fe_2S_5$	5.1	SiO_2	49.8

Required: 1. If this ore is smelted in a neutral atmosphere, without loss of sulphur except by pyritic sublimation, what grade of matte would result?

2. If this ore is roasted so that on smelting in a reducing atmosphere it is to give a matte with 45 per cent Cu, what proportion of the original sulphur must be eliminated in the roasting operation, and about what is the percentage of sulphur in the roasted ore? (Assume that in the roasted ore three-fourths of the iron will be present as Fe_2O_3 and one-fourth as Fe_3O_4.)

3. If this ore is smelted as in 2, how much SiO_2 and FeO would go into the slag, and what amount of Fe_2O_3 and $CaCO_3$ must be added to the charge, per 1,000 kg. of original ore, to make a slag with 35 per cent SiO_2, 55 FeO, 10 CaO?

245. A copper ore is composed as follows:

	Per Cent
Cu	11.0 (as Cu_2S)
Fe	33.8 (as FeS_2)
SiO_2	balance

a. This ore is smelted in a reverberatory furnace without roasting, using as fluxes, per 1,000 kg. of ore, 200 kg of $CaCO_3$ and 250 kg. of iron ore containing 85 per cent Fe_2O_3, 15 per cent SiO_2, and making a slag containing 45 per cent FeO.

b. The same ore is roasted first and then smelted in a reverberatory furnace, using per 1,000 kg. of roasted ore the same fluxes in the same amounts as before. The composition of the roasted ore yielded from roasting 100 kg. of raw ore is as follows.

	Kilograms		Kilograms
Cu_2S	9.7	Fe_2O_3	16.4
CuO	3.1	Fe_3O_4	15.9
$CuSO_4$	2.0	SiO_2	Same as in raw ore
FeS	17.0		

Required: Per 1,000 kg. of raw ore:

1. The weight and grade of the matte and the weight and percentage composition of the slag when the ore is smelted without roasting.

2. The weight and grade of the matte and the weight and percentage composition of the slag when the ore is smelted after roasting, assuming that 10 per cent of the sulphur charged into the reverberatory furnace is lost as SO_2.

3. How much iron-ore flux (instead of 250 kg.) should be used, per 1,000 kg. of roasted ore, for the slag to analyze 25 per cent SiO_2?

246. A copper blast furnace smelts ore of the following average composition:

	Per Cent		Per Cent
Cu	9	CaO	5
Fe	29	Al_2O_3	3
S	8	H_2O	6
SiO_2	31		

The flux used is limestone carrying 5 per cent SiO_2 and 95 per cent $CaCO_3$ and amounts to one-fifth of the weight of ore. The coke amounts to 12 per cent of the ore and analyzes 83 per cent C, 8 SiO_2, 4 Al_2O_3, 2 Fe, 1 S, 2 H_2O. Assume that 25 per cent of the sulphur charged is oxidized and goes into the gases as SO_2. The gas analyzes dry SO_2, 0.8 per cent; CO_2, 13; O_2, 8; N_2, 78.2. Disregard flue dust and copper in the slag.

Required: 1. The weight of matte made, per ton of ore, and its grade.

2. The weight and percentage composition of the slag.

3. The volume of the gases (dry), calculated from both the sulphur and the carbon content.

4. The volume of the blast.

247. A copper blast furnace is used for beneficiating matte, receiving per day 100 short tons of 24 per cent matte and yielding 52 per cent matte. There is charged also ore containing 60 per cent SiO_2, 10 Al_2O_3, 18 FeS, 12 Cu_2S, enough of this being used to give a slag of 40 per cent SiO_2. Assume no copper lost in the slag.

The coke used is 1 ton to every 20 tons of matte, and it carries 90 per cent C and 10 per cent SiO_2. Also, ½ ton of pure $CaCO_3$ is added per 20 tons of matte. Assume no sulphur expelled without oxidation and no CO in the gases.

Required: 1. The weight of ore charged, per day.

2. The weight of matte and of slag made, per day.

3. The volume of gases, per day, in cubic feet.

248. At the Noranda smelter, Quebec, the average daily charge to a reverberatory furnace in 1933 consisted of 1,094 short tons of calcines, 59 tons of dust (largely from the Cottrell apparatus), and 650 tons of liquid converter slag. Partial analyses of these and of the reverberatory slag are as follows:

	Calcines, per cent	Cottrell dust, per cent	Converter slag, per cent	Reverberatory slag, per cent
Cu	4.05	9.94	4.40	0.27
Fe	36.2	35.0	17.7	36.4
S	13.0	7.6		1.1
SiO_2	26.3	15.9	25.0	37.9

A low-grade matte was made, averaging 15.2 per cent Cu, 57.6 Fe, 22.5 S.

The furnace was fired with powdered coal amounting to 8.9 per cent of the calcines. Assume that the coal was 78 per cent carbon. The furnace gases analyzed 17.0 per cent CO_2, with no CO.

Assume that no SiO_2, Fe, or Cu was lost with the gases.

Required. 1. The tons of reverberatory slag made.

2. The tons of matte, calculated both from the copper and the iron contents.

3. A charge balance of the furnace with respect to Cu, Fe, S, and SiO_2.

4. The percentage of sulphur elimination in the furnace.

5. The SO_2 content of the furnace gases, in per cent.

249. A chalcopyrite ore contains 14 per cent copper as $CuFeS_2$, 22 SiO_2, and the rest FeS_2. It is smelted in a reverberatory, oil fired, with the addition of $CaCO_3$ sufficient to form a slag with 35 per cent SiO_2, 20 CaO, 45 FeO.

Assume the heat of formation of the slag as 250 Cal. per kilogram of SiO_2.

Required: 1. The weight of each compound in the charge, per 100 of ore.

2. The matte fall, per 100 of ore; and the grade of the matte.

3. The net heat generated, per 100 of ore.

250. A blast furnace smelts ore containing 23 per cent chalcopyrite ($CuFeS_2$), 50 pyrite (FeS_2), 25 SiO_2, 2 CaO. Coke is used amounting to 4 per cent of the ore, containing 90 per cent C and 10 per cent SiO_2. Pure $CaCO_3$ is used as flux.

The slag is composed of SiO_2, CaO, and FeO in the ratio 40:20:45.

Assume that one atom of S is expelled from the pyrite without oxidation, entering the gases as S_2 vapor. There is no CO in the gases.

Required: 1. The weight of slag made, per ton of ore.

2. The weight and grade of the matte, per ton of ore.

3. The volume of air required, allowing 10 per cent over theoretical.

4. The volume of the furnace gases.

5. The percentage of the heat generated in the furnace which is supplied by the combustion of the coke. (Neglect heat of formation of slag and decomposition of limestone.)

251. The ore mixture smelted in a copper reverberatory amounts to 1,000 metric tons daily, and contains the following:

	Per Cent		Per Cent
$CuFeS_2$	19	Fe_2O_3	16
FeS_2	34	CaO	3
CuO	3	SiO_2	25

Limestone (assume pure $CaCO_3$) amounting to 20 per cent of the ore is used as flux. All sulphur eliminated in the furnace is oxidized to SO_2. The matte fall is 22 per cent of the ore mixture, and its grade is 39 per cent. The gases analyze 3.6 per cent SO_2.

Assume that the heat of formation of the slag is 300 Cal per kilogram of SiO_2 contained.

Required: 1. The weight of each constituent of the slag, per day

2. The volume of the gases, per day.

3. The net heat generated in chemical reactions in the furnace, per day and per kilogram of ore.

252. Copper ore contains Cu, 15 per cent; Fe, 30; S, 33; SiO_2, 22. It is smelted pyritically to a 45 per cent matte, with $CaCO_3$ added to make 14 per cent CaO in the slag.

Heat of formation of the slag, 140 Cal. per kilogram of slag

Blast heated to 300°. Gases from furnace at 200°. Slag and matte leave the furnace at 1150°C. Assume no excess oxygen in the blast.

Required: 1. The weight of $CaCO_3$ in the charge, per 1,000 kg. of ore.

2. The total heat supplied from all sources to the furnace, per 1,000 kg of ore.

3. The total heat leaving the furnace in all forms (itemized)

4. The percentage composition of the slag.

253. Pyritic smelting was employed by the Tennessee Copper Company on a pyrite ore containing the following:

	Per Cent
Cu	2.5
Fe	40.0
S	25.0
SiO_2	25.0

The resulting matte carried 8.1 per cent Cu (NOTE: This was resmelted in another furnace to 40 per cent grade before converting)

There was charged, per day, 468 tons of ore, together with fluxes consisting of 39 tons of quartz (assume pure SiO_2) and enough $CaCO_3$ to give 1 part CaO to 3 parts SiO_2 in the slag.

The amount of blast used was 625 cu. m per minute.

Required: 1. The weight of matte and slag made, per day, and the slag ratio in terms of SiO_2:FeO:CaO, totaling 100 parts.

2. The tons of $CaCO_3$ used, per day, and the percentage of the sulphur going into the gases.

3. The percentage composition of the gases. (Assume the sulphur in the gases as SO_2, no O_2 derived from the charge, and no coke used)

4. If the ore were roasted before smelting, oxidizing nine-tenths of the sulphur (to SO_2) and nine-tenths of the iron (to Fe_2O_3), and assuming the blast furnace then to oxidize only 25 per cent of the sulphur it receives, what grade of matte would the furnace make?

5. In this case, calculate the approximate amount of coke (85 per cent C) necessary to make up for the deficiency of heat, assuming the heat requirements of the furnace to be unchanged except for the chemical reactions of the ore. Express the amount as per cent of the weight of ore. (The coke burns to CO_2.)

254. A reverberatory smelting furnace, fired with natural gas, smelts a charge composed of the following: 1,160 lb. of roasted ore analyzing Cu, 13 per cent; S, 5, CaO, 5; Fe, 28; SiO_2, 40. 280 lb. of raw ore containing Cu, 6 per cent; S, 32; Fe, 24, SiO_2, 31. 260 lb. of iron-ore flux containing Fe_2O_3, 80 per cent; SiO_2, 20. 300 lb of limestone, assumed pure $CaCO_3$.

One-fifth of all the sulphur in the charge passes off in the gases as SO_2.

Required: Per 2,000 lb. of charge:

1. A charge balance of the furnace.
2. The weight and grade of the resulting matte.
3. The weight of the slag and its SiO_2:FeO:CaO ratio (express with sum of figures equal to 100).
4. How much raw ore should have been used with the 1,160 lb. of roasted ore to make the matte grade 48 per cent?

255. Copper concentrates contain the following.

	Per Cent
Cu_2S	18
FeS_2	51
SiO_2	27
Al_2O_3	4

They are smelted in an oil-fired reverberatory furnace, using as fluxes iron ore containing 80 per cent Fe_2O_3 and 20 per cent SiO_2 and limestone of 94 per cent $CaCO_3$ and 6 per cent SiO_2.

The slag is to have the ratio SiO_2:FeO:CaO = 45:40:15, and the matte grade is to be 44 per cent.

The oil is 85 per cent C and 15 per cent H and amounts to 10 per cent of the charge.

Required: Per metric ton of concentrates.

1. The weight of each flux to be used
2. The volume of air used, and the percentage composition of the gases, allowing 10 per cent excess air over the theoretical requirement for fuel and charge

256. A copper smelter has the following materials for the blast furnace:

Roasted or oxide ore, per cent	Raw sulphide ore, per cent	Pyrite cinder, per cent
Cu 9	Cu 15	Cu 3 5
S 6	S 24	S 3
SiO_2 48	SiO_2 30	SiO_2 15
Fe 16	Fe 22	Fe 50

Limestone: CaO, 52 per cent. Coke: C, 80 per cent; SiO_2, 15.

The furnace uses coke amounting to 13 per cent of the burden One-third of the sulphur charged goes into the gases.

Required: 1. What weight of each material shall be charged to yield approximately a 48 per cent matte and a slag with a SiO_2:FeO:CaO ratio of 35:45:10, total weight of the charge without the coke to be 1,000?

2. Verify the matte grade and slag ratio resulting from the charge calculated.

257. The ores shown below are to be smelted in a reverberatory furnace, using powdered coal amounting to 15 per cent of the charge.

A. Roasted ore, per cent	*B*. Raw sulphide ore, per cent	*C*. Arsenical ore, per cent
Cu 18.0	Cu 12	Cu 18
Fe 34.0	Fe 32	As 6
S 4.5	S 34	Fe 10
SiO_2 26.0	SiO_2 12	S 15
		SiO_2 40

Assume that one-tenth of all the sulphur goes into the gases

The available flux is pure $CaCO_3$, and the coal is 85 per cent C and 15 per cent SiO_2. Assume one-third of the coal ash falls on the charge, the balance being carried out in the gases.

Required: 1. Make up a charge to yield a 48 per cent matte and a slag ratio of SiO_2:CaO:FeO = 40:20:40, charge to be in units of 10,000 lb.

2 Verify the matte grade and slag ratio resulting from the charge calculated

258. A reverberatory furnace of the Anaconda Copper Mining Company smelts 900 tons of charge per day. The materials to be smelted consist of the following.

Calcines, per cent		Pyrite Ore, per cent	
Cu	12	Cu	9
S	7	S	30
Fe	24	Fe	25
SiO_2	36	SiO_2	35
CaO	4		

Converter slag is used as a flux to furnish FeO It contains 58 per cent FeO, 30 SiO_2, 3 Cu Pure limestone is used to supply CaO.

It is desired to make a 45 per cent matte and a slag in which the ratio of SiO_2:FeO:CaO = 40:30:20.

20 per cent of the sulphur on the charge is oxidized and goes into the gases Neglect flue dust and copper loss in the slag. The furnace is fired with natural gas

Required 1. The weight of each constituent of the charge to be used, per day

2. The matte fall, in per cent of the charge.

3 Check up the slag ratio.

259. The following charge smelted in a reverberatory furnace yielded a 40 per cent matte and a slag having the ratio SiO_2:CaO:FeO = 40:20:40.

A. Roasted ore (3,340 kg.), per cent	*B*. Raw ore (520 kg.), per cent	*C*. Iron ore (120 kg.), per cent	*D*. Flux (1,020 kg.), per cent
Cu_2S 14	$CuFeS_2$ 30	Fe_2O_3 80	$CaCO_3$ 80
FeS 20	FeS_2 20	SiO_2 12	$MgCO_3$ 15
Fe_2O_3 21	SiO_2 50	Al_2O_3 8	Fe_2O_3 3
Fe_3O_4 14			SiO_2 2
SiO_2 24			
Al_2O_3 7			

Required: 1. Calculate the weight and composition of matte and slag that would result if this charge were used in a blast furnace, using 12 per cent of coke (C, 85 per cent and SiO_2, 15), with a sulphur elimination of 40 per cent.

2. Calculate (using algebraic methods) the composition of a 5,000-kg. charge to make the same 40 per cent matte and slag of the same composition as in the reverberatory furnace.

260. A copper ore contains 14 per cent copper combined as Cu_2S, 15 per cent SiO_2, and the rest FeS_2. It is smelted in a reverberatory furnace, oil fired, together with copper concentrates containing 35 per cent Cu_2S, 40 SiO_2, 25 FeS_2. Fluxes used are iron ore containing 80 per cent Fe_2O_3, 20 SiO_2, and pure $CaCO_3$

Heat of formation of the slag, 200 Cal. per kilogram of SiO_2.

Required: 1 Using 100 kg. of the ore, what weight of concentrates, iron-ore flux, and $CaCO_3$ must be charged to make a 48 per cent matte and a slag having the ratio $SiO_2:CaO:FeO = 35:20:45$?

2. The net heat generated or absorbed, in Calories per 100 kg of the ore.

261. In converting copper matte, the following reactions take place:

$$2FeS + 3O_2 = 2FeO + 2SO_2$$
$$Cu_2S + O_2 = 2Cu + SO_2.$$

The air is blown in at 40°C and 1,200 mm total pressure The gases come out at 1200°C., 770 mm No fuel is used, and no excess air The air includes 45 mm. of water vapor

The matte contains 48 per cent Cu

Required: For 10 metric tons of matte·

1. The volume of dry air, at standard conditions, that must be blown in, and its weight.

2. The volume of moist air, at given conditions, and its weight.

3. The volume of issuing gases, at given conditions.

4. The heat carried out by the gases

262. A copper converter is charged with 25 tons of 48 per cent matte and blown down to blister copper. The flux used carries Cu, 8 per cent; Fe, 16; S, 8; SiO_2, 60; and the slag carries 28 per cent SiO_2, 63 FeO, 4 CuO After the first slag is poured, additional matte is charged, amounting to the weight of the FeS oxidized from the first charge. Assume all Fe in the flux not as $CuFeS_2$ to be as Fe_2O_3 The blister copper formed carries 98 per cent Cu and 0.5 per cent S. Air is supplied at the rate of 120 cu. m. per minute.

Required: 1. The total weight of flux used and of slag made.

2. The weight of blister copper formed.

3. The cubic meters of blast used.

4. The time occupied by:

a. The first slagging period.

b. The second slagging period.

c. The blister-forming period.

263. A converter is charged with 25,000 kg. of 36 per cent matte. There is added as flux 2,000 kg. of dry ore carrying 70 per cent SiO_2, 15 FeS_2, and 10 Cu_2S, and the converter is blown until a slag is formed in which the ratio $FeO:SiO_2$ is 72:28. The slag is then poured off, another 2,000 kg. of flux added, and the blow resumed, this being repeated until not enough FeS remains to require another 2,000-kg. addition. 15,000 kg. more matte is then poured in, and the operations are repeated. On the last partial blow, just enough flux is added to slag all the remaining iron. The white metal is then blown down to blister copper. The blowing engine supplies 110 cu. m.

of air per minute. Assume that none of this air is used in oxidizing the atom of S liberated from FeS_2 in the flux and that no free O_2 or SO_3 goes from the converter.

The gases escape from the converter at an average temperature of 1100°C. in the slagging period, 1200°C. in the blister-forming period. Neglect heat entering in the blast.

Required: 1. The number of partial blows in the slag-forming period.

2. The total blowing time of each of the two stages of the blow.

3. The net heat generated, per minute, after deducting heat in the gases, in each of the two periods.

264. A converter blows to blister copper a charge of 20 short tons of matte containing 46 per cent copper. There is used as flux ore carrying 4 per cent Cu_2S, 16 FeS, 80 SiO_2. The slag is to be 29 per cent SiO_2. Assume that there is no copper in the slag.

Blast is supplied at the rate of 3,200 cu. ft per minute (standard conditions).

Required. 1 The weight of flux necessary.

2. The volume of blast required for the entire blow.

3. The blowing time of each of the two stages, and the heat generated, per minute, in each.

4. The percentage of SO_2 in the gases during each stage

5. Assuming all the flux added at the start, after how many minutes blowing will the matte contain 60 per cent copper?

265. The slag from a copper converter contains the following:

	Per Cent
SiO_2	32
Al_2O_3	1
CaO	8
FeO	59

The flux carries 75 per cent SiO_2, 5 FeS_2, 2 Cu_2S. The matte charge is 40 tons carrying 34.3 per cent Cu. The flux is added in batches of 3,000 kg.; the converter is blown to slag of the above composition after each addition and the slag poured off before the next batch is added.

The blast has a volume of 100 cu m. per minute measured at the conditions under which it enters the blowing engine, 20°C., 660 mm. It is compressed to a pressure of 5,000 kg per square meter (at 20°C.), gage pressure.

Required 1 The time of each partial blow

2. The number of partial blows and the weight of flux to be added for the last partial blow to produce a slag of the same composition as in the others.

3. The total time for blowing the charge to blister copper

4. The power required to furnish the blast.

266. At the Granby smelter, Anyox, B.C., the blast furnaces produce a 15 per cent copper matte. This is blown to a grade of 35 per cent in one converter, then transferred to another and blown to blister copper.

Assume the same rate of blast supply in both converters, and neglect any addition of copper in the flux or loss of copper in the slag.

Heat generated in slag formation = 153 Cal. per kilogram of FeO slagged.

Required: 1. The relative blowing times in the two converters

2. The grade to which the matte would have to be blown in the first converter in order to make the blowing times equal in the two converters.

3. If 10 tons of 15 per cent matte is blown to 35 per cent matte in 2 hr. and then transferred, what is the amount of heat generated, per minute, in each converter?

267. At the Kosaka smelter, Japan, the converters treat per charge 8 tons of 37 per cent matte. Blast is furnished at the rate of 90 cu. m. per minute. Before adding flux a preliminary blow of 10 min. is given to produce a magnetite coating, which analyzes as follows:

	Per Cent
Fe_3O_4	74.8
FeO	4.8
CuO	5.1
Unoxidized constituents	15.3

Assume that this is entirely corroded by the end of the slag-forming stage. The converter slag carries the following:

	Per Cent
Fe_3O_4	31.7
FeO	39.7
SiO_2	15.8
CuO	5.0

The flux carries Cu_2S, 2.4 per cent; FeS, 28; SiO_2, 53.

The blister copper is 98.8 per cent Cu and 0.3 per cent S.

The converter gases carry no free oxygen.

Required: 1. The weight of magnetite coating produced.

2. The weight of flux required.

3. The weight of slag made.

4. The weight of blister copper, and the percentage of copper recovery.

5. The blowing time of each stage.

6. The volume and percentage composition of the converter gases.

268. A copper converter is charged with 35 tons of 48 per cent matte and 10 tons of flux (Cu, 8 per cent; Fe, 16; S, 8, SiO_2, 60) and makes 21.4 tons of slag (SiO_2, 28 per cent; FeO, 63; CuO, 4). Fe in flux not as $CuFeS_2$ is Fe_2O_3; the blister copper carries 98 per cent Cu and 0.5 per cent S. Slagging period, 231 min.; blister-forming period, 110 min. The blast used is 42,600 cu. m.

The matte is charged at 1050°C., the flux at 0°, and the blast is at 30°. Assume that during the blow the slag and matte are at the same temperature and that the gases leave the converter at the temperature of the bath. Assume the specific heat of matte 0.14 for all compositions; melting point of matte, 1000°; melting point of slag, 1120°; specific heat, 0.25. Heat content of liquid matte at melting point, 205 Cal. per kilogram; of liquid slag at melting point, 300 Cal. per kilogram. Heat of formation of the slag is 376 Cal. per kilogram of SiO_2. Assume the specific heat of blister the same as for pure copper.

Required: A heat balance of the converter at the end of the slagging period and at the end of the blow.

269. A copper converter, lined with magnesite, contains 50 short tons of 35 per cent matte at 1100°C. If allowed to stand, the matte cools at the rate of 2°C. per minute. Specific heat of melted matte, 0.14.

10,000 lb. of cold silica sand is added and blowing at once commenced. Assume that no free oxygen escapes from the converter; gases at the same temperature as the matte and slag.

Slag desired, 30 per cent SiO_2 and 70 per cent FeO.

Heat content of this slag at 1100°, 300 lb.-cal. per pound.

Specific heat of the slag, 0.25.

Heat of combination of the SiO_2 with FeO, 375 lb.-cal. per pound of SiO_2.

Heat in liquid FeO or FeS at 1100°, 215 lb.-cal. per pound.

Required: 1. What is the net heat left in the converter (neglecting radiation and conduction losses), per cubic foot of air blown in?

2. At what rate, in cubic feet per minute, must air be supplied to keep the temperature at 1100°C.?

3. At what rate may air be supplied, assuming that when the slag has reached the desired composition its temperature (and that of the matte) will not be over 1350°C.?

CHAPTER XVI

ELECTROLYTIC PROCESSES

Metallurgical processes employing electrolysis may be divided into those in which aqueous solutions are electrolyzed, carried on at temperatures seldom exceeding 60°C., and those in which fused salts are electrolyzed, carried on at high temperatures. The first class includes electrolytic refining, in which a soluble (or largely soluble) anode is used, and electrolytic deposition of metals from leaching solutions, in which an insoluble anode is used. It also includes electroplating, in which the anode may be either soluble or insoluble. The second class includes the usual methods of producing aluminum, magnesium, and other chemically strong metals.

Calculations concerning electrolytic processes will be concerned chiefly with the following factors or with related ones which follow directly from these:

1. The amount of metal theoretically deposited by a given current or, conversely, the number of amperes theoretically required to deposit a given amount of metal
2. The current efficiency and the actual amount of deposition
3. The voltage required to carry on the electrolysis.
4. The power required to produce a given amount of metal (a combination of items 1, 2, and 3).

Faraday's laws of electrolysis apply without exception in all cases of electrolysis. As a result of these laws, item 1 above can be established with certainty; it can be stated definitely that the quantity of electrolytic action is a function only of the current and the time and that, for every 96,500 amp.-sec. (coulombs) passed through the electrolyte, one chemical equivalent (in grams) of substance is liberated at the cathode and an equivalent amount of substance is liberated at the anode.

The current efficiency is defined as the actual quantity of a particular substance deposited or dissolved, divided by the theoretical quantity liberated in accordance with Faraday's laws. The point of the matter is not that the current may do less than Faraday's laws demand, but that part of the metal after being deposited is then lost by some action not a part of the electrolysis itself, or that part of the electrolytic action of the current is expended in depositing or dissolving some substance other than the one with which the process is primarily concerned. The latter alternative is likely to be the greater factor in the reduction of current efficiency; in fact, it nearly always occurs in electrolysis to a greater or less extent. There are few cases where the current efficiency at the cathode even approaches closely to 100 per cent, *i.e.*, few cases in which all the current is depositing the particular metal which it is the object of the process to deposit; nearly always part of it is depositing some other metal or hydrogen, or part of the metal deposited is being redissolved or lost in some other manner. Similar conditions prevail at the anode. The silver coulometer is an example of the current operating at 100 per cent efficiency—all the current passing performing the same chemical action.

Current efficiency may also take into account loss due to some current not passing through the electrolyte. For example, in electrolytic refining the total current may be measured by ammeters placed in the main line and the theoretical deposit calculated from this amount. Some of the current, however, may not pass through the electrolyte at all but may be by-passed or may leak away through other conductors.

The chemical equivalent in grams, or the gram equivalent, is given by the atomic weight divided by the valence.

The following example illustrates the use of Faraday's laws and the factor of current efficiency:

Example 31

Calculate the thickness of chromium plating deposited in 2½ min. at a current density of 180 amp. per square foot and a current efficiency of 14 per cent.

Solution: The number of coulombs flowing is 180 × 2.5 × 60 = 27,000 per square foot. The solution is of CrO_3, in which chromium has a valence of 6. The weight of Cr theoretically deposited is therefore:

$$\frac{27{,}000}{96{,}500} \times \frac{52}{6} = 2.42 \text{ g. per square foot.}$$

The actual deposit is $0.14 \times 2.42 = 0.34$ g. per square foot $= \frac{0.34}{929}$, or 0.00037 g. per square centimeter.

The density of Cr is 7.1 g. per cubic centimeter. The thickness is therefore $\frac{0.00037}{7.1} = 0.000052$ cm. = 0.0000205 in.

Expressed as a formula, the amount of metal deposited

$$= \frac{\text{at. wt./valence}}{96{,}500} \times \text{no. of amp.} \times \text{no. of sec.}$$

$$= \frac{\text{gram equiv. wt.}}{96{,}500} \times It.$$

The weight of metal deposited at 100 per cent efficiency by unit current in unit time is known as its *electrochemical equivalent.* The electrochemical equivalent of silver in metric units is 0.001118 g. per ampere-second, a quantity used by international agreement to define the value of the ampere. Since the valence of silver is 1, the amount of any other metal deposited is given by $\frac{\text{at. wt./valence}}{107.9} \times 0.001118 \times It$. This method, or rather this form of the first method, since obviously it is directly equivalent, is often used instead of the first form above.

Composition of Cell Voltages.—The voltage of an electrolytic cell does not directly affect the amount of deposit; it does so only in so far as it affects the current. And in most cells there is no proportional relation between the amount of the voltage and the amount of the current. This is because the voltage-current relation given by Ohm's law, $I = \frac{E}{R}$, applies to only one of several factors in the total voltage of the cell.

Calculations in electrolytic processes having to do with the current, as outlined above, are simple and at the same time indispensable for design and control. Calculations dealing with the voltage, however, are more complex. They include a number of different factors of greater or less uncertainty, and in general it is not possible to calculate or predict the voltage requirement with satisfactory accuracy. Usually it is best to construct an experimental cell and make voltage measurements. However, it is often useful to calculate certain components of the voltage, and it is altogether desirable to study the principles involved in voltage calculation both as a possible tool and for an understanding of the different factors. These will be discussed in some detail.

The e.m.f. necessary to cause the current to pass through an electrolytic cell must accomplish the following:

1. It must overcome the ohmic resistance of the electrolyte. This portion of the voltage follows Ohm's law, $E = IR$, in which R is the resistance of the electrolyte as a conductor, analogous to the resistance of a copper wire or any conductor of the first class. Let this component of the total voltage be denoted by the symbol E_C.

2. Since current cannot pass through an electrolyte without performing electrolysis, the e.m.f. must supply the change of energy involved in the chemical reaction taking place in the cell. This *reaction potential* is directly equivalent to the decrease of free energy accompanying the chemical change involved in the cell reaction. This portion of the voltage has nothing to do with Ohm's law. While the change of free energy varies with the temperature at which the chemical reaction takes place, the variation is, practically speaking, not a large one; and, for all electrolyses of aqueous electrolytes, this component may practically be considered a constant for any given cell so long as the chemical reaction in the cell does not change. This component, as shown below, includes not only the energy corresponding to the heat of the reaction but also that corresponding to a temperature change in the cell. Let this component of the total voltage be denoted by E_{RP}.

3. The e.m.f. must take care of polarization in the cell. Usually the greater part of the polarization voltage in industrial electrolytic cells is accounted for by the voltage required to liberate a gas at either electrode in addition to the reaction potential. Actually, the polarization voltage will include some voltage required to overcome concentration polarization and often other small polarizations as well; but these are usually relatively small, and ordinarily when no gas is liberated in a cell the polarization component may be neglected. It should be noted that this discussion applies to the practical calculation of voltage in a metallurgical cell and does not include all factors necessary in a rigid consideration of e.m.f. in electrolysis. In dealing with cells having considerable polarization due to solid films or other causes, this should be separately specified. Since practically the major part of the polarization voltage is that due to gas, we shall let this component of the total voltage be denoted by E_G.

In addition to the three components just enumerated, the voltage applied to an electrolytic cell is usually increased measurably by the resistance of contacts. In electrolytic copper refining, this contact resistance is a relatively large part of the total voltage, perhaps 15 per cent. In electrolytic copper refining about an equal portion (*i.e.*, about 15 per cent) of the total line voltage is required by the metallic conductors. Another special factor in copper refining is that the resistance of the cell is increased by the accumulation of slimes on the anode. These factors are of great importance in figuring power consumption in copper refining, but they do not belong to a general consideration of the internal voltage of the electrolytic cell itself. Contact resistance in most cases is a relatively small factor. While it tends to obey Ohm's law, it cannot be assumed to do so entirely. It depends chiefly on the design of the contact, its cleanness, and the weight or pressure at the contact. An effort is made to keep it as low as possible; and if it is not low it is usually an indication of dirt, faulty design, or some other condition that may be remedied. Evidently this factor is not adaptable to calculation: it must be determined by experiment or estimated when thought to be too large to neglect for the purpose of the calculation.

Summarizing the above, and denoting the total cell voltage by E_T, we have:

$$E_T = E_C + E_{RP} + E_G.$$

To these components should be added any additional polarization voltage as well as contact voltages when these are known to be important in magnitude.

Determination of each of these three principal voltage components will now be considered, with examples.

1. E_C, the voltage of conduction, is determined by $E = IR$ when R is known for the electrolyte. R, the total resistance over a given section, must usually be calculated from r, the resistivity. The resistivity is the resistance in ohms of a section of unit length and one square unit in cross section.

Since the resistance varies directly with the length of path of flow and inversely with the cross section of the path of flow, it follows that $R = r\frac{l}{s}$, in which r is the resistivity, l is the length of the path, and s its cross-sectional area.

The common metric unit section is the centimeter cube, *i.e.*, 1 cm. long and 1 sq. cm. in cross section. It will be observed that this is not the same thing as a cubic centimeter, in which the length may be anything so long as the product of the three dimensions is 1. A section 100 cm. long and 0.1 by 0.1 cm. in cross section is a cubic centimeter, but its resistance is 10,000 times that of a centimeter cube. The common English unit section is the inch cube. The resistivity per centimeter cube is 2.54 times the resistivity per inch cube.

In applying the above formula for calculating the resistance of a conducting section from its dimensions, *viz.*,

$$R = r\frac{l}{s},$$

it is important to use for s the values for the same cross section over which I, the current in the expression $E = IR$, is taken. If the current density is 180 amp. per square foot and 180 is taken as the value of I, the value of s must be 1 sq. ft. reduced to square inches or square centimeters (144 or 929), depending on whether r is given in English or metric units. Neglect to observe this correlation of I and s may result in errors of several thousand-fold. If the correlation is observed, it is immaterial what size section is taken; *i.e.*, it is immaterial what is taken for s so long as the current over that same section is taken for I.

Evidently knowledge of the value of r is required. In problem work, r is often given, but in practice it is often necessary to determine r. In some cases this is best done by direct experimental measurement, as by the method of Kohlrausch, or R may be measured with a portion of the electrolyte in a standard tube for which the value of $\frac{s}{l}$, called the "cell constant," is known. Then $r = R\frac{s}{l}$. Often, however, it is convenient to determine r by reference to tables of resistivities of solutions. This, of course, requires knowledge of the strength of the electrolyte (*i.e.*, its concentration) if it is a solution of a single salt and of its composition and concentration if it is a mixed solution. In the latter case the necessary data may be difficult or impossible to find in any tables.[1] The conductivity of a solution of more than one salt is not an additive function of conductivities contributed by each of the salts dissolved, nor is the conductivity determinable by weighted averaging.

In any case, in determining r it is necessary to correct the value for the temperature at which the electrolyte is to be used, since resistances of solutions change rapidly with change of temperature. Tables of conductivities or resistivities usually give the values at 18°C. and include a column for the temperature coefficient. In using the tables it is important to bear in mind that the conductivities of electrolytes *increase* with rise of temperature. Table LIII, page 425, gives the conductivities of a number of important solutions at different concentrations.

The length of path of current flow, l, is the distance between electrodes in the cell and is readily determined. The value to be taken for s, however, is not always so evident. With large plates close together, s will be approximately the same as the size of the plates or the size of the larger plate if the plates are nearly the same size. If one plate is much smaller than the other, s will be somewhat less than the size of the larger plate but will be much above the mean between the two sizes. If the plates are relatively far apart, s will be close to the size of the cross section of the cell or tank, even if this is much greater than the size of the plates.

2. In many cases E_{RP} is a much larger component than E_C, and its calculation involves more uncertainty. This "chemical voltage" of the cell is made up of the difference between the e.m.fs. of the two electrodes; it is the difference between two single potentials. Consequently, in a cell like that of the copper coulometer (two copper electrodes in a solution of $CuSO_4$), the value of E_{RP} will be zero because the chemical action at the anode is equal and opposite to that at the cathode. This is nearly true also in electrolytic copper refining, where the cathode is pure copper and the anode about 99 per cent copper. In most cells, however, this is not the case, and E_{RP} depends on the chemical reaction of the cell. Experimentally, knowledge of E_{RP} may be approached by measurement of single potentials; but unless these are measured with normal current flowing, they may be considerably changed by polarization. Nernst's equation, $E = \frac{RT}{nF} \ln \frac{p}{\pi}$, throws light on the nature of the electrode potential but is not serviceable for calculation in practice owing to lack of knowledge of the values of π, the electrolytic solution pressure, and p, the osmotic pressure.

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[1] For discussion and tabulated data on conductivities of electrolytes used in copper refining, see E. F. Kern and M. Y. Chang, "Conductivity of Copper Refining Electrolytes," *Trans. Am. Electrochem. Soc.*, **41**, 181–196 (1922); and S. Skowronski and E. A. Reinoso, "The Specific Resistivity of Copper Refining Electrolytes and Method of Calculation," *ibid.*, **52**, 205–231 (1927).

The most readily available method for calculation of E_{RP} is by means of Thomson's rule and the Gibbs-Helmholtz equation. The latter equation is:

$$E = \frac{U}{njF} + T\frac{dE}{dT},$$

in which E is the e.m.f. of the cell, U (or $-\Delta H$) is the heat of the reaction of the cell in calories; n is the valence change, or number of chemical equivalents of substance reacting; j is the constant for changing joules to calories ($= 0.239$); F is the number of coulombs of electricity passing through the cell ($= 96{,}500$ for each chemical equivalent of substance); and T is the absolute temperature of the electrolyte.

Ignoring for the moment the third term of this equation, the expression becomes:

$$E = \frac{-\Delta H}{23{,}060n}.$$

Expressing this in words: To find the reaction voltage of a cell, calculate the heat of the reaction in calories and divide by 23,060 times the number of chemical equivalents (as shown by the total valence change) taking part in the reaction. This reaction voltage is the e.m.f. of a cell when no current is flowing, *i.e.*, the open-circuit e.m.f.

This expression, known as *Thomson's rule*, may be used to approximate the value of the E_{RP} component in many practical metallurgical processes. The ease of application of the rule makes it very useful for at least a first approximation; but the results must be taken with caution for the reason that this rule ignores the final term as derived by Gibbs and Helmholtz. The value of the final term is not often negligible, and in a few cases it is even larger than the middle term. It may be either positive or negative. It expresses the change in value of E accompanying change of temperature in the cell while the reaction is taking place. It is the temperature coefficient of the cell (change in E per degree) multiplied by the absolute temperature. Thomson's rule assumes that the change in free energy in the cell (corresponding to E) is equal to the *total* energy change, whereas in most cells the free-energy change does not equal the total energy change but there is in addition some energy either derived from or given up to the surroundings in the form of heat. This additional energy causes the change in temperature (either cooling or heating) denoted by $\frac{dE}{dT}$, the temperature coefficient.

While the term $T\frac{dE}{dT}$ is less readily usable in practice owing to lack of knowledge of the value of $\frac{dE}{dT}$, some data on temperature coefficients are available, and it is sometimes possible to apply this correction to Thomson's rule.

There is, however, a more generally usable method of applying the Gibbs-Helmholtz equation for calculation of reaction potentials. It may be shown that the term $T\frac{dE}{dT}$ in the equation is equivalent to $T\frac{\Delta S}{23{,}060n}$, where ΔS is the entropy change in the reaction. This question is discussed in Chap. XXIV, where it is brought out that $nFE = -\Delta F$, in which ΔF is the free-energy change of the reaction, and $\Delta F = \Delta H - T\Delta S$. Hence:

$$E = -\frac{\Delta H}{nF} + T\frac{\Delta S}{nF}.$$

Tables are available giving the values of S for many substances. From these, ΔS may be found by summating them just as in obtaining ΔH.

From the foregoing discussion it is evident that Thomson's rule would give the correct value of E_{RP} only if the free-energy change of the reaction ΔF were used in place of the heat of the reaction ΔH. Accordingly, ΔF should be used for this calculation whenever it is available. As an example, the reaction potential for electrolysis of water as calculated from the heat of the reaction ($-\Delta H = 68{,}370$ cal.) would be:

$$E = \frac{68{,}370}{23{,}060 \times 2} = 1.48 \text{ volts.}$$

But the correct value obtained from the free-energy change ($-\Delta F = 56{,}484$ cal., calculated on page 381) is:

$$E = \frac{56{,}484}{23{,}060 \times 2} = 1.225 \text{ volts.}$$

Since the principles involved in the use of ΔS and ΔF have not yet been discussed, we shall in the balance of this chapter confine calculation of reaction potential to the use of Thomson's rule.

3. The value of E_G cannot be calculated. It must simply be estimated from experience or data on similar electrodes and the same gases. It is a relatively large quantity and its value depends on many factors, especially on the kind of gas liberated, the kind of metal or alloy used for the electrode, and the current density. Estimates may be several tenths of a volt in error.

An example will now be given illustrating calculations of voltage in a metallurgical process involving all three of the components E_C, E_{RP}, and E_G. This problem also includes calculation of power requirement.

Example 32

In a plant for extracting copper from $CuSO_4$ by electrolysis, the average resistivity of the solution is 5 ohms per centimeter cube; electrodes 4 cm apart; gas voltage

at the anode, 0.5 volt; current density, 165 amp. per square meter; voltage drop, cathode plate to bus bar, 0.05 volt, anode plate to bus bar, 0.10 volt. Ampere efficiency of deposition, 85 per cent. Current per tank, 1,000 amp.

Required: 1. The voltage absorbed in overcoming the ohmic resistance of the electrolyte.

2. The voltage absorbed in chemical reaction, on the assumption of Thomson's rule.

3. The voltage drop, anode to cathode.

4. The voltage drop, bus bar to bus bar.

5. The weight of copper deposited, per day, per tank.

6. The kilowatts, per tank.

7. The kilowatt-hours used, per kilogram of copper deposited.

Solution: Here $r = 5$, $l = 4$, $s = 1$ sq. m. (= 10,000 sq. cm.) when $I = 165$ amp.

$$R = r\frac{l}{s} = 5 \times \frac{4}{10,000} = 0.002 \text{ ohm.}$$

$$E_C = IR = 165 \times 0.002 = 0.33 \text{ volt (1).}$$

The reaction of the cell is:

$$CuSO_4 + H_2O = Cu + H_2SO_4 + O.$$

The heat of this reaction is $\Delta H = -200,640 - 68,380 + 212,400 = -56,620$ Cal (using the heats of formation in dilute solution, from Table XLVI, page 419).

$$E_{RP} = \frac{56,620}{23,060 \times 2} = 1.23 \text{ volts (2).}$$

$$E_T = E_C + E_{RP} + E_G = 0.33 + 1.23 + 0.50 = 2.06 \text{ volts (3).}$$

$$2.06 + 0.05 + 0.10 = 2.21 \text{ volts (4).}$$

$$\frac{0.85 \times 1,000 \times 86,400}{96,500} \times \frac{63.6}{2} \div 1,000 = 24.2 \text{ kg. of Cu per day per tank (5).}$$

$$2.21 \times 1,000 = 2,210 \text{ watts} = 2.21 \text{ kw. per tank (6).}$$

$$2.21 \times 24 = 53.0 \text{ kw.-hr. per day per tank.}$$

$$\frac{53.0}{24.2} = 2.19 \text{ kw.-hr. per kilogram of Cu deposited (7).}$$

Electrolytic Refining.—The calculation of total voltage or amperage for a plant will depend on the system of electrical connections. The electrodes within each tank are connected in parallel in most cases, so that the voltage drop across the entire tank is the same as that between any pair of plates in the tank. The tanks are then connected in series,

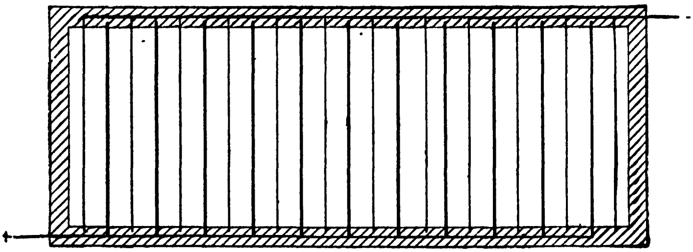

FIG. 9.—The multiple system (electrode plates in parallel).

with such number in the circuit as can be supplied by a generator of suitable voltage. This is the "multiple system" of connections; unless information is given to the contrary, it may be assumed to be the method used in any metallurgical plant. One important exception is the employment of the "series system" at two of the large copper refineries. In this system the tanks and also the plates within the tanks are connected in series. Here each plate acts as anode on one side and cathode on the other In the multiple system there are separate anodes and cathodes, all the anodes being connected to one bus bar and all the cathodes to another. The cathodes receive a deposit on both sides. The two methods are illustrated in Figs. 9 and 10.

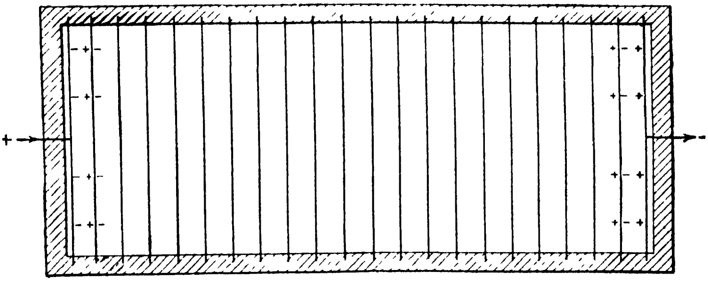

FIG. 10.—The series system (electrode plates in series).

Current density is usually stated in amperes per unit of active cathode surface.

Example 33

The Raritan Copper Works electrolytic refinery has a capacity of 480,000,000 lb. of copper annually (365 days), figured at a current density of 17.3 amp. per square foot of cathode surface.

Each tank has 31 cathodes and 30 anodes, multiple system. The cathodes measure $30\frac{1}{4}$ by $38\frac{1}{2}$ in. and are entirely immersed in the electrolyte

The average distance from anode to cathode surface is 1.35 in The voltage per tank is 0.24. The tanks are connected in four separate circuits, with one generator to each circuit.

Required: 1. The number of tanks if all were in regular operation, with 93 per cent current efficiency.

2. The resistivity of the electrolyte, assuming 50 per cent of the voltage drop used in overcoming electrolyte resistance.

3. The voltage and amperage of each generator.

4. The power cost per pound of copper produced, assuming power at $60 per kilowatt-year.

Solution: Cu deposited by 1 amp. in 365 days at 93 per cent efficiency = $0.93 \times 1 \times \frac{365 \times 24 \times 60 \times 60}{96,500} \times \frac{63.6}{2}$ = 9,670 g. = 21.3 lb.

Amperes per tank: Area of cathode (2 sides) = $2 \times \frac{30.25 \times 38.5}{144}$ = 16.17 sq. ft.

$17.3 \times 16.17 \times 30 = 8{,}392$ amp. (30 is used instead of 31 because the two end cathodes receive a deposit on one side only.)

$\frac{480{,}000{,}000}{21.3 \times 8{,}392} = 2{,}685$ tanks (1) (The total number required would be greater owing to making of starting sheets at lower current density)

$0.50 \times 0.24 = 0.12$ volt $= E_C$.

$R = \frac{E}{I} = \frac{0.12}{17.3}$, or 0.0069 ohm for 1 sq. ft section $= 0.0069 \times 144 \times 6.45 = 6.43$ ohms for 1 sq. cm.

$l = 1.35 \times 2.54 = 3.43$ cm.

$r = R\frac{s}{l} = 6.43 \times \frac{1}{3.43} = 1.87$ ohms per centimeter cube $= 0.74$ ohm per inch cube (2).

$2{,}685 \div 4 = 671$ tanks per circuit.

$671 \times 0.24 = 161$ volts for each generator.

8,392 amp. for each generator (3).

Total power $= 161 \times 8{,}392 \times 4 \div 1{,}000 = 5{,}400$ kw.

$5{,}400 \times \$60 = \$324{,}000$ per year.

$\frac{324{,}000 \times 100}{480{,}000{,}000} = 0.068$ ct. per pound of copper (4)

Deposition from Leaching Solutions.—In depositing copper electrolytically from a leaching solution, the use of insoluble anodes greatly alters the voltage requirement. Instead of the deposition at the cathode being practically balanced by the dissolving action at the anode, copper is deposited at the cathode and oxygen liberated at the anode. This introduces a gas voltage and also a reaction potential corresponding to the reaction

$$CuSO_4 + H_2O = Cu + H_2SO_4 + O.$$

Example 34

In 1932 the electrodeposition plant of the Chile Exploration Co at Chuquicamata, Chile, contained in the section having lead-antimony anodes 572 tanks, each tank having 63 anodes and 62 cathodes The size of cathodes was 3 by 4 ft and the current density 12.7. The ampere efficiency of deposition was 86 per cent.

The oxygen gas voltage was 0.42 volt.

Required: 1. Assuming 0.35 volt for conduction, contacts, etc., what was the voltage per tank?

2. What would be the power cost per pound of copper deposited, assuming power at $150 per kilowatt-year?

3. Estimate the annual saving in power cost by having the electrolyte at approximately 36 instead of 18°C

Solution: As in Example 32, the heat of the reaction is $-56{,}620$ Cal.

By Thomson's rule:

$$E_{RP} = \frac{56{,}620}{23{,}060 \times 2} = 1.23 \text{ volts.}$$

Total voltage then $= 0.35 + 1.23 + 0.42 = 2.00$ (1).

Copper deposited per year $= 0.86 \times 12.7 \times 12 \times 2 \times \frac{365 \times 86{,}400}{96{,}500} \times \frac{63.6}{2} =$ 2,720,000 g. per cathode.

2,720 × 62 × 572 × 2.2 = 212,000,000 lb. total.
Amperes per tank = 12.7 × 12 × 2 × 62 = 18,900.
Power = 572 × 2.00 × 18,900 ÷ 1,000 = 21,600 kw.
Power cost = 21,600 × \$150 = \$3,240,000 per year.

$$\frac{3{,}240{,}000 \times 100}{212{,}000{,}000} = 1.53 \text{ cts. per pound of copper (2).}$$

The resistivity of the electrolyte would differ considerably from that of the previous example and in the absence of data must be assumed. A reasonable assumption would be 2.5 ohms per centimeter cube. If this is the value at 36°, what would it be at 18°?

The conductivity $= \frac{1}{2.5} = 0.40$. Referring to conductivity tables (*e.g.*, Landolt and Bornstein),[1] it is found that, for H_2SO_4 with a conductivity of 0.40, the conductivity increases by 0.013 of itself for each rise of 1°C. Neglecting the effect of $CuSO_4$, which is small compared with that of the H_2SO_4 and would be of the same order, there is indicated an approximate change of 18 × 0.013, or 23.4 per cent. That is, the conductivity at 18° would be about $^{100}/_{123} \times 0.40 = 0.325$ The resistivity then would be $\frac{1}{0.325} = 3.08$ ohms, an increase of $3.08 - 2.5 = 0.58$ ohms. The total voltage would then be increased by $\frac{0.58}{2.50} \times (0.5 \times 0.35) = 0.041$ volt. Since a voltage of 2.00 gave a power cost of \$3,240,000 a year, the indicated saving at 36° as compared with 18° is $\frac{0.041}{2.00} \times \$3{,}240{,}000 = \$66{,}000$ (3). (This result indicates a difference of about \$3,700 per year for a difference of 1°C in the electrolyte temperature.)

Soluble Anodes of Mixed Composition.—Two cases of electrolysis have been considered, that of an insoluble anode and that of a soluble anode of the same composition as the cathode deposit. A third case is frequently encountered in practice, *viz.*, that of a soluble or partly soluble anode of composition different from that of the cathode deposit. Two important questions arising are: At what rate does the current cause the anode of mixed composition to dissolve, and what is the effect on the voltage requirement?

When the anode consists partly of soluble elements and partly of insoluble material, the current must be satisfied in accordance with Faraday's laws by electrochemical solution of the soluble elements. The insoluble material mechanically forms slime, and the total weight of anode used is accordingly increased. An anode four-fifths soluble and one-fifth insoluble would be used up at five-fourths, or 1¼, times the rate of a completely soluble anode; but the amount of substance actually dissolving (forming soluble compounds) would be the same in each case, as required by Faraday's laws. For anodes containing different soluble elements, however, the word "amount" must be interpreted as amount in chemical equivalents; accordingly, the actual *weight* of anode going into solution depends on what elements compose it.

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[1] See also Table LIII, p 425

When an anode containing several elements is attacked by the current (or, more strictly speaking, by solute-forming anions), there is a selective action which makes the chemically stronger elements tend to dissolve in preference to the chemically weaker. This selective action is modified by the relative amounts of different elements present. Thus, in copper refining, silver does not dissolve because silver is below copper in the electropotential series of metals (*i.e.*, it is chemically weaker), and also there is relatively little of it present. Its solution as Ag_2SO_4 is retarded and prevented by the presence of Cu. Nickel and iron, which are stronger than copper, dissolve readily, forming $NiSO_4$ and $FeSO_4$; but they do not appreciably retard the solution of copper as $CuSO_4$, because there is relatively so little of them present. Thus it happens in electrolytic refining processes that all the elements which dissolve at all usually dissolve at about the same rate in proportion to the percentages of them present, and there is relatively little of that tendency to leave a pitted anode which would result from the solution of some elements faster than others. For purposes of calculation it may usually be assumed that the anode dissolves "uniformly," meaning that the unused part remains of the same percentage composition as the original anode.

This assumption having been made, the percentage of the total current which is acting on each soluble element may be calculated readily from Faraday's laws; it is obvious that this percentage division of the current is different from the percentage composition of the anode, because it takes more current to dissolve a gram of one kind of element than to dissolve a gram of another. There is also calculated readily the number of ampere-seconds used in dissolving 1 g. of anode and hence the weight of anode corroded by a given current.

With regard to the voltage, it is obvious that that percentage of the current which is forming $CuSO_4$ is operating at a different reaction voltage from the portion which is forming $NiSO_4$ or something else. Thus the total E_{RP} for the cell is made up of different parts, the total being the weighted sum of the various components. It is usually best to calculate E_{RP} at the cathode, then E_{RP} at the anode, subtracting to get E_{RP} for the cell. This will be made more clear by an example.

Example 35

Gold bullion refined by the Wohlwill process contained Au, 89 per cent; Ag, 8; Pb, 1; Cu, 2. Au goes to $AuCl_3$, Ag to AgCl, Cu to CuCl, Pb to $PbCl_2$. The gold is deposited pure at 100 per cent efficiency. The anodes corrode uniformly, and no chlorine is set free The current passing is 500 amp

Required: 1. The weight of gold deposited, per day.

2. The weight of anode consumed, per day

3. The depletion of the electrolyte in gold.

4. The reaction voltage of the cell, as based on the assumption of Thomson's rule.

Solution:

$$\frac{500 \times 86,400}{96,500} \times \frac{197.2}{3} = 29,420 \text{ g. of gold deposited per day (1).}$$

Since the anode is 89 per cent Au, an approximation of the weight of the anode consumed is given by $\frac{29,420}{0.89} = 33,060$ g. This method, however, is theoretically incorrect and in many cases may not give a sufficiently close approximation. It assumes that the weight of Au dissolved equals the weight of Au deposited, which is not true. The correct method follows:

Ampere-seconds required to dissolve 1 g. of anode.

$$\begin{aligned}
&\text{For Au: } 0.89 \times \left(96,500 \div \frac{197.2}{3}\right) &= 1,305 \text{ amp.-sec}\\
&\text{For Ag: } 0.08 \times (96,500 \div 107.9) &= 72\\
&\text{For Cu: } 0.02 \times (96,500 \div 63.6) &= 30\\
&\text{For Pb: } 0.01 \times \left(96,500 \div \frac{207.2}{2}\right) &= 9\\
&\qquad 1.00 \text{ g. of anode requires} &\overline{1,416} \text{ amp.-sec}
\end{aligned}$$

$$\frac{500 \times 86,400}{1,416} = 30,510 \text{ g. corroded (2)}$$

$$0.89 \times 30,510 = 27,150 \text{ g. of Au dissolved}$$

$$29,420 - 27,150 = 2,270 \text{ g. depletion (3).}$$

$$(\text{Au, Cl}_3)\ (aq) = 32,750 \text{ cal.} = \frac{32,750}{23,060 \times 3} = 0.473 \text{ volt.}$$

This is the reaction voltage at the cathode. At the anode, $AuCl_3$ is formed and $\frac{1,305}{1,416}$, or 92.2 per cent, of the current is used in doing this. This will generate $0.922 \times 0.473 = 0.436$ volt. Similarly voltage is generated by formation of AgCl, CuCl, and $PbCl_2$.

Voltage generated at the anode.

$$\begin{aligned}
(\text{Au, Cl}_3)\ (aq) &= \frac{1,305}{1,416} \times \frac{32,750}{23,060 \times 3} &= 0.436 \text{ volt}\\
(\text{Ag, Cl}) &= \frac{72}{1,416} \times \frac{30,600}{23,060} &= 0.067\\
(\text{Cu, Cl}) &= \frac{30}{1,416} \times \frac{34,300}{23,060} &= 0.032\\
(\text{Pb, Cl}_2)\ (aq) &= \frac{9}{1,416} \times \frac{79,120}{23,060 \times 2} &= 0.011\\
&\qquad\qquad \text{Total} &= \overline{0.546} \text{ volt}
\end{aligned}$$

Total $E_{RP} = 0.44 - 0.55 = -0.11$ volt (or 0.11 volt generated) (4).

NOTE: The same result would be obtained by carrying the computation through on a thermochemical basis, getting the result in calories per chemical equivalent, and then dividing by 23,060. The reactions of the cell could be written as follows:

$$\begin{aligned}
AuCl_3 + 3Ag &= Au + 3AgCl; &\quad \Delta H &= -\ 59,050 \text{ cal.}\\
AuCl_3 + 3Cu &= Au + 3CuCl; &\quad \Delta H &= -\ 70,150\\
2AuCl_3 + 3Pb &= 2Au + 3PbCl_2; &\quad \Delta H &= -171,860
\end{aligned}$$

Problems

270. A copper refinery using the series system has 400 tanks, each containing 40 anodes 2 by 3 ft. The current density is 16 amp. per square foot. The anodes are $\frac{9}{16}$ in. thick at the start and are spaced at 2 in. center to center. The electrolyte has a resistivity of 10 ohms per inch cube. The current efficiency is 72 per cent.

Required: 1. The copper output of the plant, per day.

2. The voltage used in overcoming the resistance of the electrolyte, per tank.

3. The time required to convert an anode into pure copper.

271. The copper refinery at Great Falls, Mont., has 1,440 tanks, each containing 25 anodes and 26 cathodes. The cathodes are 38 by 29 in. The current density is 27 8 amp. per square foot and the current efficiency 90 per cent. The tanks are arranged in six separate circuits, each with a generator operating at 1,130 kw. output. The multiple system is used. Of the voltage absorbed, assume that 65 per cent is used in overcoming the resistance of the electrolyte and 35 per cent lost in contacts and other losses. The distance from anode to cathode surface is 5 cm.

Required: 1. The capacity of the plant, in kilograms per day and tons per year.

2. The increase in thickness of a cathode, per day.

3. The voltage absorbed, per tank.

4. The resistivity of the electrolyte, in ohms per centimeter cube

272. The copper refinery of Canadian Copper Refiners, Ltd., at Montreal East is designed to operate at a current density of 17 amp. per square foot. The starting sheets are 37½ in. square and weigh 11 lb. There are 432 tanks used for making cathodes, each containing 42 anodes spaced 4½ in. center to center, and 43 cathodes. Assume the current efficiency 94 per cent.

Each anode is used 33 days, and two cathodes are made for each anode. Assume that the anode dissolves at a rate equivalent to 100 per cent current efficiency and that nine-tenths of its thickness is dissolved before removal from the tank. The voltage per tank is 212 mv , of which 65 per cent is required for the resistance of the electrolyte.

Required: 1. The annual capacity of the plant (in pounds), including starting sheets, operating 360 days.

2. The number of hours required to make a starting sheet, at the same current density and efficiency, and its thickness in inches.

3. The resistivity of the electrolyte, in ohms per centimeter cube.

273. The following data are from the tank house of the United States Metals Refining Company, Carteret, N. J. The multiple system is used

Number of tanks, 1,824.

Plates per tank, 37 anodes and 38 cathodes.

Size of cathodes, 38 by 37 in , entirely immersed.

Average distance, anode surface to cathode surface, 1.125 in

Voltage per tank, 0.21 volt, of which 40 per cent is used in overcoming the resistance of the electrolyte.

Current density, 15.4 amp per square foot of cathode surface.

Ampere efficiency of deposition, 96 per cent.

Average composition of the electrolyte:

Cu: 38 g. per liter.
Free H_2SO_4: 190 g per liter.

Average temperature of electrolyte, 55°C.

Required: 1 The weight of copper deposited, per day, in pounds

2. The number of kilowatt-hours used, per pound of copper deposited

3. The growth in thickness of each cathode, per day.

4. The resistivity of the electrolyte, calculated from the resistance and dimensions.

5. The resistivity of the electrolyte, calculated from the conductivity of the H_2SO_4 and $CuSO_4$ mixture.[1] NOTE: This result will be lower than that of 4 because it disregards nickel and other impurities in the electrolyte.

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[1] See first reference in footnote, p. 263.

274. A series copper refinery uses tanks measuring inside 16 ft by 60 in deep by 62 in. wide. Each tank contains 610 anode plates, each 12 in wide, arranged in fives across the tank, making 122 large anodes End anodes are against the ends of the tanks. Separate plates are 0.40 in thick

The solution stands ½ in. above the upper edge of the plates. The lower ends are 2½ in. from the bottom of the tank.

Voltage per tank, 16. Current density, 20 amp per square foot. Ampere efficiency, 75 per cent.

Required: 1. The average distance between plates

2 The thickness of copper deposit, per day

3. The resistivity of the solution

4. The number of tanks required to furnish 550 short tons of copper, per day

5. The electric power (kilowatts) required to run the plant

275. A copper-refining plant uses an electrolyte containing 11 per cent $CuSO_4.5H_2O$, 12 H_2SO_4, with an electrical resistivity of 2 ohms per centimeter cube

The series system is used, with 40 plates in each tank Working distance, 5 cm. Current density, 200 amp. per square meter. Immersed area of one side of each plate, 90 by 120 cm. Thickness, 3 cm

Assume ampere efficiency 80 per cent Assume anode scrap 10 per cent, of which 5 per cent is in the lugs and 5 per cent in the body of the plate

Assume 100 per cent efficiency of corrosion, and calculate it as if it were pure copper dissolving

Required 1. The current used, per tank

2. The working voltage, per tank.

3. The thickness of deposited copper, per day.

4. The time for corrosion of the anodes.

5. The weight of copper under treatment, per tank.

276. An electrolytic copper refinery uses a current density of 16 amp. per square foot. Each tank contains 30 anodes and 31 cathodes. The immersed area of each cathode (one side) is 37 by 38 in The voltage per tank is 0.25 volt (multiple system). Thickness of anodes at starting, 1.3 in. Ampere efficiency of deposition, 95 per cent. The entire plant contains 1,600 tanks in operation. Resistivity of the electrolyte at the temperature used, 1.65 ohms per centimeter cube. The anodes are run down to a thickness of 0.10 in. The distance from anode to cathode is 2 in.

The electrolyte tends to build up in copper, due to re-solution of some copper at the cathode and chemical solution of a corresponding amount at the anode. This excess is removed by crystallization of $CuSO_4.5H_2O$, the amount of copper contained in this copper sulphate being equal to 2.5 per cent of the output of cathode copper.

Required: 1. The amperes per tank, and the power in kilowatts required to operate the tanks.

2. The proportion of this power converted into heat in the electrolyte.

3. The output of the plant, per day, in kilograms.

4. The gain in thickness of each cathode, per day

5. The number of days an anode will be in the tank.

6. What portion of the 5 per cent loss in current efficiency is represented by re-solution of copper at the cathode? (Assume that an equal amount is dissolved chemically at the anode.)

7. How many liters of sulphuric acid (specific gravity 1.84, equal to 93.2 per cent H_2SO_4) must be added, per day, to keep up the acidity of the electrolyte?

277. The International Smelting & Refining Co. (Raritan Copper Works) electrolytic refinery has 2,685 tanks, each containing 30 anodes and 31 cathodes. The multiple system is used, and the current density is 17.3 amp. per square foot of cathode surface. The cathodes are $30\frac{1}{4}$ by $38\frac{1}{2}$ in. The current efficiency is 93 per cent.

The electrolyte contains 3.75 per cent copper and 17 per cent free H_2SO_4. Its resistivity is 1.7 ohms per centimeter cube. The average distance from anode to cathode surface is 3.5 cm. The cathodes are withdrawn after 13 days' deposition, the anodes after 26 days. Temperature of electrolyte, 58°C.

Assume power cost at $60 per kilowatt-year.

Required: 1. The daily capacity of the plant in pounds of refined copper.

2. The weight and thickness of a finished cathode.

3. The voltage drop in the electrolyte between each pair of plates.

4. Allowing an additional 0.12 volt per tank for contact resistances, etc., what is the power cost annually and per pound of copper produced?

5. What would be the annual power cost if the electrolyte contained no free acid?

6. What would be the annual power cost, approximately, if the electrolyte were at 25°C. instead of 58°C.?

278. A copper refinery, multiple system, uses anodes weighing 225 kg. and containing Fe, 2 per cent; Zn, 1; Ni, 0.5; and Cu, 96.3. The tank contains 24 anodes and 25 cathodes. Anodes are 4 cm. thick, cathodes 1 mm.; each has an immersed area of 75 by 80 cm. The tank is 260 cm. long. The specific resistance of the solution is 2.0 ohms. Anodes are changed every 30 days; cathodes every 15 days. The current efficiency of the cell is 94 per cent. Current density, 200 amp. per square meter. Number of tanks, 1,200.

Required: 1. The amperes passing through each tank.

2. The theoretical output of copper, per day, in the plant.

3. The weight of anode consumed, per day.

4. The voltage drop required to overcome the resistance of the electrolyte.

5. The thickness of the cathodes when drawn.

6. The amount (per cent) of anode scrap made (neglect chemical solution by H_2SO_4).

279. An experimental plant at the Baltimore Copper Smelting & Rolling Company electrolytically refined anodes of black copper containing:

	Per Cent
Cu	68.2
Pb	10.4
Ni	12.4
Insoluble elements	9.0

The anodes dissolved uniformly.

The electrolyte was of the ordinary sulphuric acid type, and the cathode deposit may be taken as pure copper.

The tank received 6,000 amp., and the current efficiency was 90 per cent, the loss being due to chemical re-solution of copper already deposited and other causes.

At the beginning of the run, the electrolyte in the tank contained 95,000 g. of copper. At the end of 48 hr., it contained 102,000 g. of copper.

Required: 1. The gain in weight of the cathodes in 48 hr.

2. The weight of anodes consumed in this time (assume all the current used in dissolving).

3. The weight of copper redissolved from the cathodes in this time (assume equal amounts dissolved chemically by H_2SO_4 from anodes and cathodes).

4. The reaction voltage in the tank.

280. A plant for recovering the copper from leaching solutions has 390 tanks in continuous operation. The multiple system is used, with lead anodes and copper cathode starting sheets. 1,000 amp. passes through each tank. The current density is 150 amp. per square meter.

The resistivity of the solution coming to the tanks is 15 ohms per centimeter cube; leaving the tanks, 5 ohms per centimeter cube. Distance from anode to cathode surface, 3 cm. Voltage absorbed in contacts and bus bars, 0.1 volt per tank. Gas voltage, both electrodes combined, 0.55 volt.

The ampere efficiency is 86 per cent.

Required: 1. The pounds of cathode copper produced, per day.

2 The voltage absorbed in the chemical reaction

3. The average total voltage, per tank.

4. The average total power required for the plant.

5. The weight and volume of oxygen and of hydrogen set free, per day, assuming that 12 per cent of the current is decomposing water.

281. The tank house for recovery of copper from the leaching solutions at Chuquicamata, Chile, contained, in 1932, two divisions, one using lead-antimony anodes and one using Chilex anodes. The former had 668 tanks (including tanks for the production of starting sheets) and the latter 430 tanks. The former had 63 anodes and 62 cathodes per tank, used a current density of 12.7 amp. per square foot, and deposited at a current efficiency of 86 per cent. The latter had 56 anodes and 55 cathodes per tank, used a current density of 8.0, and had a current efficiency of 87 per cent The cathodes in each measured 3 by 4 ft.

Assume the average resistivity of the electrolyte as 2 2 ohms per inch cube. The voltage per tank with the lead-antimony anodes was 1.96 and with the Chilex anodes 2 24 The distance from anode surface to cathode surface was 1 4 in Allow 0.2 volt for contact resistances.

Assume that power cost $150 per kilowatt-year.

Required 1 The total output of the plant at full capacity, in pounds per year (365 days).

2. The gas voltage on the lead-antimony anodes and on the Chilex anodes.

3 The annual saving in power cost if the Chilex anodes were replaced by lead-antimony.

282. In the electrodeposition plant of the New Cornelia Copper Company, Ajo, Ariz., there were 152 tanks, each with 77 cathodes. The cathodes were 42 by 42 in. The space from anode to cathode surface was 2 in. In March, 1918, the plant produced 3,152,800 lb. of copper, the current depositing 0.92 lb. per kilowatt-hour. The average resistivity of the electrolyte was 5 ohms per centimeter cube The voltage per tank was 2.08 volts. Assume 0.10 volt absorbed in contacts. The tank house was divided electrically into two circuits, each with one generator.

Required: 1. The current density, in amperes per square foot

2. The current efficiency.

3. The cubic meters of oxygen generated per day, and the amount of H_2SO_4 formed, in liters of 60°Bé. equivalent. (1 liter of 60°Bé. acid contains 1.334 kg. H_2SO_4)

4. The amperes and voltage required of each generator.

5. The voltage per cell absorbed in electrolyte conduction, in decomposition, and in gas overvoltage.

6. The power cost per pound of copper produced, at $200 per kilowatt-year.

7 The annual saving in power cost if it were feasible to deposit the copper from a CuCl solution at the same current efficiency, assuming all voltages unchanged except the decomposition voltage.

283. A Betts electrolytic lead refinery makes 200 metric tons of refined lead per day. Current density used, 200 amp. per square meter, parallel system. Anodes and cathodes (immersed portions), 50 by 80 cm. 20 anodes and 21 cathodes in each tank.

Ampere efficiency of deposition, 93 per cent. Volts used per tank, 0.4. Distance from anodes to cathodes, 3 cm.

Required: 1. The average number of tanks in operation.

2. The power required of the generator.

3. The resistivity of the electrolyte.

284. The electrolytic lead refinery of the Consolidated Mining & Smelting Co. at Trail, B.C., has a capacity of 200,000 short tons of lead annually. There are 24 anodes and 25 cathodes per tank. The lead starting sheets measure 3 ft. 3 in. by 2 ft. 2¾ in. by 0.028 in. and are removed from the tank after 3 days' deposition at a current density of 19.4 amp. per square foot, current efficiency of 93 per cent. Two cathodes are made for each anode. The anodes are 99.0 per cent lead. Anode scrap, 33 per cent.

The tanks are 8 ft. 9½ in. long by 2 ft. 6½ in. wide by 3 ft. 6 in. deep. Assume that the electrolyte fills the tank to within 4 in. of the top. The electrolyte carries 72 g. of lead per liter. The submerged part of the anode measures 30⅛ by 26¼ in. The tanks are connected in two circuits, each requiring 200 volts.

Required: 1. The number of tanks in operation at full capacity.

2. The weight and thickness of a finished cathode.

3. The average weight of lead under treatment in the plates and electrolyte, and its value at 6 cts. per pound.

4. The resistivity of the electrolyte, assuming that 70 per cent of the voltage is used in overcoming the electrolyte resistance.

285. Silver bullion refined by the Balbach-Thum process has the following composition:

	Per Cent
Ag	94
Au	3
Cu	2
Pb	1

Gold remains undissolved, while copper and lead enter the electrolyte as nitrates The slimes are 88 per cent Au, 12 per cent Ag.

The size of the cathode plate is 2 by 4 ft. The distance from the anode to the cathode is 4.5 in. The current density is 24 amp. per square foot.

The plant has 180 cells in series. The current efficiency is 93 per cent at the cathode, 100 per cent at the anode.

The voltage of each cell is 3.7 volts, of which 80 per cent is used in overcoming the resistance of the electrolyte.

Required: 1. The annual production in troy ounces of silver, running 360 days a year, for the whole plant.

2. The resistivity of the electrolyte, in ohms per centimeter cube.

3. The weight of anode, in kilograms, needed for the plant every 24 hr., and the weight of slimes produced in this time.

4. The voltage generated or absorbed (which?) as reaction voltage in each cell

286. The Moebius silver refining plant of the American Smelting & Refining Company at Barber, N. J., in 1940 consisted of 180 tanks, with five cathodes and four rows of five anodes each in each tank. The cathodes were 12½ by 20 in., and the current density was 33 amp. per square foot. The current efficiency was 93 per cent at the cathode and 100 per cent at the anode. The voltage was 2.5 volts per tank Assume that power cost $60 per kilowatt-year.

The fineness of the anodes was 975 Ag, 6 Au, 19 Cu. The anode scrap to be remelted was 18 per cent. At the start of the operation the electrolyte carried 32 g. of Ag and 30 g. of Cu per liter. The electrolytic tank held 150 liters of solution.

Assume the price of silver 71.1 cts. per ounce (United States government price for domestic silver in 1940); of gold, $35 per ounce.

Required: 1. The silver output of the plant, per day, in troy ounces.

2. The power cost, per day.

3. The percentage of the value of the silver used for power cost.

4. The weight of anode material required daily.

5. The interest charges, per day, on the precious metals passing through the tanks, at 5 per cent per annum.

6. The e.m.f. contributed to the circuit by the anodic solution of copper instead of silver.

7. The silver and copper content of the electrolyte at the end of the day's operation.

287. A gold bullion has a composition of Au, 91 per cent; Ag, 6; Cu, 2; Pb, 1 per cent. It is refined by the Wohlwill process in an electrolyte of $AuCl_3$ plus HCl. The tank receives 100 amp.; efficiency of deposition, 100 per cent.

The anodes corrode uniformly.

Required: 1. The weight of gold deposited, per day.

2. The weight of anode corroded, per day.

3. The net reaction voltage generated or absorbed (which?).

288. In the gold-refining plant of the U.S. Metals Refining Co., Carteret, N. J., the tanks measure 12 by 12 by 14 in. deep, and are filled with electrolyte to within 3 in. of the top. The electrolyte carries 100 g. of gold per liter. The starting sheets of rolled gold are 12 by 2.5 by 0.005 in., while the anodes are 9 by 4.5 by $\frac{3}{8}$ in. The anodes average 975 fine in gold. Each tank contains four anodes and five rows of two cathodes each. The current is 100 amp. per square foot of anode surface (disregarding edges) and the voltage 3.8 volts per cell, of which 90 per cent is used in overcoming the resistance of the electrolyte.

Assume that the distance from the end cathodes to the edge of the tank is the same as to the next anode.

Required: 1. The daily output of gold when four tanks are in operation, at the current efficiency of 100 per cent, and its value at $35 per ounce.

2. The ounces of gold under treatment (in plates and electrolyte) in four tanks, and its value.

3. The resistivity of the electrolyte, in ohms per inch cube.

289. Gold bullion refined by the Wohlwill process contained Au, 85 per cent, Ag, 11; Pb, 1.8; Cu, 2; Pt, 0.2. Au goes to $AuCl_3$, Ag to AgCl, Cu to CuCl, Pb to $PbCl_2$, Pt to $PtCl_4$. The gold is deposited pure at 100 per cent ampere efficiency. The anodes corrode uniformly, and no chlorine is set free. Current, 500 amp. total depositing gold.

The electrolyte becomes depleted of gold, the deficiency being made up in one of the following ways:

a. Part of the bullion is dissolved in aqua regia, the HNO_3 boiled off, and the solution added to the electrolyte.

b. Part of the current is diverted to an auxiliary lead cathode surrounded by HCl only, separated from the main electrolyte by a porous diaphragm.

Required: 1. The weight of gold deposited, per day.

2. The weight of anode corroded, per day.

3. In *a*, the amount of bullion, in proportion to the total consumed, that is dissolved in aqua regia.

4. In *b*, the proportion of the total current diverted to the lead cathode.

5. The voltage absorbed or generated as reaction voltage in *a* and in *b*.

290. A Siemens & Halske gold-precipitating plant, no longer operated, consisted of 20 tanks through which the solution flowed, each tank containing 40 sq. m. of cathode surface and using 400 amp. of current. 1,000 metric tons of cyanide solution was circulated through the tanks per day, its gold content being reduced from $12.15 per ton to $0.18 per ton, figured at the old standard of $20.67 per ounce. The gold is present in the solution as $NaAu(CN)_2$.

Assume that all the current not depositing gold decomposes NaCN. All (CN) liberated in the tanks combines with the anodes, forming $Fe_5(CN)_{12}$. Anodes 94 per cent Fe, rest insoluble.

Required: 1. The ampere efficiency of gold deposition.

2. The thickness of gold deposit, per day.

3. The weight of anode consumed, per day.

4. The volume of hydrogen liberated, per day.

291. An experimental plant is designed to separate copper and nickel electrolytically from scrap monel metal. The monel metal is melted and cast into anodes analyzing:

	Per Cent
Ni	67
Cu	28
Fe	5

These are hung in a tank of acidified $CuSO_4$ containing 1,125 kg. of copper, and a current of 5,700 amp. is passed through until the electrolyte carries copper and nickel in equal amounts. The anodes dissolve approximately uniformly, owing to passivity of iron and nickel. Assume that copper deposits at 100 per cent efficiency.

The electrolyte is now run into a second tank having lead anodes, and 2,000 amp is passed until the deposit of copper is no longer pure, 90 per cent of the copper content having then been removed.

After cementing out the remaining copper, the electrolyte is run to a third tank, also having lead anodes, and pure nickel is deposited.

The voltage of conduction in the first tank is 0.1; in the second, 0.2, in the third, 0.3 volt. The gas voltage at the lead anodes is 0.45. In addition, 0.2 volt is absorbed at contacts in each tank.

The current efficiency in the third tank is 90 per cent, the other 10 per cent decomposing water.

Required. 1 The time of electrolysis in the first and second tanks

2. The reaction voltage in each tank

3. The total voltage across each tank.

292. *a.* A plating works uses a high *pH* nickel sulphate bath, saturated with boric acid; the latter constituent is not decomposed in the electrolysis. Platings are made with a cathode current density of 24 amp. per square foot for 45 min. The current efficiency of nickel deposition is 95 per cent and of nickel corrosion at the anode 90 per cent. (Assume that 5 per cent of the current liberates H_2 at the cathode, while 10 per cent liberates O_2 at the anode)

Required: 1. The thickness of the nickel plating, in inches and in millimeters.

2. The volumes of O_2 and of H_2 liberated in 45 min , per square foot.

3. The grams of H_2SO_4 formed in the bath in 45 min , per square foot

b. With a low *pH* bath, using a current density of 800 amp. per square meter, and at 75 per cent ampere efficiency of deposition, how long will it take to deposit 0.001 in. of nickel?

293. Copper wire of 0.050 in. diameter is to be tinned electrolytically with a tin coating 0.0003 in thick, a current density of 44 amp. per square foot being used. Assume that tin is liberated from the compound Na_2SnO_3 The current efficiency is 94 per cent.

Required: 1. The current, in amperes per foot of wire.

2. The time of plating.

3. The pounds of tin in the coating, per 1,000 ft. of wire.

4. The percentage increase in the diameter and in the weight of the wire.

5. The value of the copper and of the tin in 1,000 ft. of coated wire. (Assume copper at 12 cts., tin at 52 cts. per pound.)

294. The electrolytic zinc plant of the Anaconda Copper Mining Company at Great Falls, Mont., has 1,152 tanks, each containing 28 anodes and 27 cathodes. The cathodes, of aluminum, are 45 in. wide and are immersed to a depth of 24 in. The thickness of both anodes and cathodes is $\frac{3}{16}$ in. The current density is 30 amp. per square foot. The average current efficiency is 93 per cent; assume that the other 7 per cent decomposes water into hydrogen and oxygen.

Lead anodes are used, with an oxygen gas voltage of 0.40; there is a hydrogen gas voltage at the cathode of 0.10. The average resistivity of the electrolyte is 2.8 ohms per inch cube. The anodes are spaced at 3 in. center to center. Allow 0.20 volt for contact resistances.

Required: 1. The annual capacity of the plant, in pounds.

2. The growth in thickness of each cathode in 24 hr.

3. The cubic feet of oxygen and of hydrogen liberated in the plant in 24 hr.

4. The voltage per tank and the kilowatt-hours consumed, per pound of zinc deposited.

295. An electrolytic zinc plant is to be designed to turn out 100 metric tons of zinc per day. From laboratory experiments, an average ampere efficiency of 85 per cent can be expected. Assume that 15 per cent of the current decomposes water into hydrogen and oxygen. Cathodes receive deposit on both sides, immersed surface of each, 0.90 sq. m.; current density, 300 amp. per square meter; working voltage, 3.5 per tank. Each tank contains 20 cathodes and 21 anodes.

Required: 1. The necessary number of tanks in continuous operation.

2. The net electric power required in the whole plant.

3. The thickness of the deposit stripped from the cathode, assuming it stripped every 24 hr.

4. The heat, in Calories, generated as sensible heat in each tank, per minute. (Assume that the e.m.f. producing heat is the tank voltage minus the reaction voltage minus 0.5 volt for gas polarization.)

296. At the electrolytic zinc plant of the Sullivan Mining Company, Kellogg, Idaho, there are three circuits of 150 tanks each. Each circuit has two motor-generator sets connected in parallel, each set delivering 4,000 amp. at 500 volts. The current density is 100 amp. per square foot. The immersed area of each cathode is 27 by 21 in. The starting cathodes are of aluminum; they are removed and stripped at intervals of 8 to 12 hr.

The distance from anode to cathode surface is $\frac{5}{8}$ in. Assume that 20 per cent of the average tank voltage is used in overcoming the resistance of the electrolyte.

The average current efficiency is 90.5 per cent.

Required. 1. The capacity of the plant, in pounds per year.

2. The number of cathodes, per tank.

3. The kilowatt-hours used, per pound of zinc.

4. The maximum and minimum thickness of zinc stripped from the cathode plates.

5. The average resistivity of the electrolyte, in ohms per inch cube.

CHAPTER XVII

HYDROMETALLURGY

Leaching practice varies widely between different plants. The details of procedure depend so greatly on the nature of the ore treated that there cannot be any standardization of the degree which applies in many pyrometallurgical operations. Even in the latter there is rarely such a thing as closely standardized practice between different plants, and even at single plants details of operation are altered frequently as raw materials change or improvements are developed.

Leaching practice often involves a complex series of interrelated steps. Problems dealing with leaching give an instructive view of the relations from a quantitative standpoint. Examples will be given in this chapter illustrating copper leaching at the largest hydrometallurgical plant in the world and others illustrating the cyanide process for gold and silver. It is in general notable in leaching processes that the weights of solution involved are several times the weight of the ore and also that large amounts of wash water are required. Descriptions of leaching processes found in the literature often contain a multitude of data, the proper selection and application of which may be the principal difficulty in a calculation. Sometimes data given are conflicting when analyzed, and sometimes those necessary for determining a particular point may be lacking.

Example 36

Following is the log of a typical leaching charge at Chuquicamata, Chile.
Charge: 8,212 tons of ore carrying 1.6 per cent Cu.

SOLUTION ADDED

Tons	Cu, per cent	H_2SO_4, per cent	Cl, per cent
3,300	3.5	6.8	0.2
2,600	2.2	7.0	0.1
2,100	2.5	5.0	0.1
3,300	3.6	4.4	0.3
3,300	3.1	3.3	0.3
3,400	2.2	2.0	0.2
3,300	0.8	0.6	0.1
600			

SOLUTION DRAWN OFF

Tons	Cu, per cent	H_2SO_4, per cent	Cl, per cent
2,700	4.8	3.8	0.5
2,300	4.2	5.2	0.3
3,300	3.6	4.8	0.2
3,300	3.5	4.3	0.3
3,300	3.1	3.3	0.3
3,300	2.2	1.9	0.2
2,800	1.1	0.8	0.1

600 tons of the last wash solution goes to precipitation tanks for removal of the copper by cementation on scrap iron (94 per cent Fe). All the remaining solution is reated for precipitation of the Cl content by the reaction $CuCl_2 + Cu = 2CuCl$. This CuCl is then dissolved in brine and cemented on scrap iron.

Required: 1. The percentage extraction from the ore.

2. What percentage of the copper lost is undissolved in the tailings, and what percentage in solution discarded with the wet tailings?

3. The weight of scrap iron required to cement the copper from the discarded wash solution.

4. The weight of scrap iron required to cement the copper from the CuCl.

5. The total scrap iron used, per ton of copper extracted.

6 What percentage of the cement copper produced will be needed for dechloridizing?

Solution

Tons of Cu in Solution Added	Tons of Cu in Solution Drawn Off
$0.035 \times 3{,}300 = 115.5$	$0.048 \times 2{,}700 = 129.6$
$0.022 \times 2{,}600 = 57.2$	$0.042 \times 2{,}300 = 96.6$
$0.025 \times 2{,}100 = 52.5$	$0.036 \times 3{,}300 = 118.8$
$0.036 \times 3{,}300 = 118.8$	$0.035 \times 3{,}300 = 115.5$
$0.031 \times 3{,}300 = 102.3$	$0.031 \times 3{,}300 = 102.3$
$0.022 \times 3{,}400 = 74.8$	$0.022 \times 3{,}300 = 72.6$
$0.008 \times 3{,}300 = 26.4$	$0.011 \times 2{,}800 = 30.8$
$0 \times 600 = 0$	
Total 21,900 547.5	Total 21,000 666.2

Cu extracted $= 666.2 - 547.5 = 118.7$ tons

Cu in ore $= 0.016 \times 8{,}212 = 131.4$ tons.

Percentage extraction $= \frac{118.7}{131.4} = 90.4$ per cent (1).

Solution discarded with tailings $= 21{,}900 - 21{,}000 = 900$ tons

Cu in this $= 0.011 \times 900 = 9.9$ tons.

Total Cu lost $= 131.4 - 118.7 = 12.7$ tons.

$\frac{9.9}{12.7} = 78$ per cent lost in solution.

$100 - 78 = 22$ per cent undissolved (2).

Cu in discarded wash solution $= 0.011 \times 600 = 6.6$ tons. Most of this will be present as $CuSO_4$, some as $CuCl_2$. In either case, 56 Fe is required to precipitate 64 Cu, the reactions being:

$CuSO_4 + Fe = Cu + FeSO_4$.

$CuCl_2 + Fe = Cu + FeCl_2$.

Fe required $= \frac{56}{64} \times 6.6 = 5.8$ tons.

But Fe will also be consumed by the H_2SO_4 in the solution: $H_2SO_4 + Fe = FeSO_4 + H_2$.

$H_2SO_4 = 0.008 \times 600 = 4.8$ tons.

Fe required $= \frac{56}{98} \times 4.8 = 2.7$ tons.

Total Fe $= 5.8 + 2.7 = 8.5$ tons, or $\frac{8.5}{0.94} = 9.0$ tons of scrap iron (3).

The Cl precipitated will be that in the solution drawn off (except 600 tons) minus that left unprecipitated. The amount of the latter is indicated by the Cl content of the solution added.

Cl in Solution Drawn Off	Cl in Solution Added
$0.005 \times 2,700 = 13.5$	$0.002 \times 3,300 = 6.6$
$0.003 \times 2,300 = 6.9$	$0.001 \times 2,600 = 2.6$
$0.002 \times 3,300 = 6.6$	$0.001 \times 2,100 = 2.1$
$0.003 \times 3,300 = 9.9$	$0.003 \times 3,300 = 9.9$
$0.003 \times 3,300 = 9.9$	$0.003 \times 3,300 = 9.9$
$0.002 \times 3,300 = 6.6$	$0.002 \times 3,400 = 6.8$
$0.001 \times 2,200 = 2.2$	$0.001 \times 3,300 = 3.3$
Total $= 55.6$	Total $= 41.2$

Cl precipitated $= 55.6 - 41.2 = 14.4$ tons.

Cu needed for dechloridizing $= \frac{64}{2 \times 35.5} \times 14.4 = 13.0$ tons.

Total Cu in CuCl $= 2 \times 13.0 = 26.0$ tons

$$Fe + 2CuCl = 2Cu + FeCl_2.$$

Fe needed $= \frac{56}{128} \times 26.0 = 11.4$ tons Scrap iron $= \frac{11.4}{0.94} = 12.1$ tons (4). $12.1 + 9.0 = 21.1$ tons of scrap iron used.

$21.1 \div 118.7 = 0.18$ ton per ton of Cu extracted (5)

Cement Cu produced $= 26.0$ from CuCl $+ 6.6$ from wash solution $= 32.6$ tons

Per cent needed for dechloridizing $= \frac{13.0}{32.6} = 40.0$ per cent (6)

CYANIDATION

In the cyanide process for extraction of gold and silver, the ore is leached with a very dilute solution of sodium cyanide. Gold and silver are then precipitated from the solution, usually by means of zinc. The chemical reactions governing the dissolving and precipitation are now considered to be the following:

Elsner's equation:

$$2Au + 4NaCN + O + H_2O = 2NaAu(CN)_2 + 2NaOH.$$

Precipitation equation:

$$NaAu(CN)_2 + 2NaCN + Zn + H_2O = Au + Na_2Zn(CN)_4 + H + NaOH.$$

In these equations, Ag may be substituted for Au and KCN for NaCN.

The equations may be used for calculation of the requirements of NaCN and zinc. However, since NaCN will react with other compounds present, the actual consumption of cyanide is considerably greater than is called for by the equations; the same is true of the zinc. The actual consumption of cyanide is usually obtained from the NaCN contents of the solution before and after leaching, in the same manner as in calculating the recovery of metal. This is illustrated in the following example:

Example 37

A cyaniding mill treats per month 2,000 tons of ore containing 12.27 oz. of silver per ton, with no gold. There is obtained 6,800 tons of solution, from which the silver is precipitated with zinc shavings. The extraction of silver by the leaching is 87 per cent, and the solution after precipitation still carries 0.15 oz. of silver per ton

The consumption of NaCN in leaching is 2 43 lb per ton of ore, and the leaching solution at the start carries 0.25 per cent NaCN. The solution entering the zinc boxes contains 0.68 lb. of NaCN per ton. The consumption of zinc is 1 34 lb per ton of ore.

Required: 1. The percentage of the silver in the ore that is recovered in the precipitate.

2. The amounts of leaching solution and of wash water used

3. The percentage of the NaCN consumed that is actually used in dissolving silver

4. The percentage of the zinc consumed that is actually used in precipitating silver

Solution

$$\begin{array}{lll} \text{Ag in solution before precipitation} = 12.27 \times 2{,}000 \times 0.87 & = & 21{,}350 \text{ oz.} \\ \text{Ag in solution after precipitation} = 0\ 15 \times 6{,}800 & = & \underline{\ 1{,}020} \\ \hfill \text{Ag recovered} & = & 20{,}330 \text{ oz} \end{array}$$

$$\text{Percentage recovery} = \frac{20{,}330}{24{,}540} = 82.8 \text{ per cent (1).}$$

$$\begin{array}{lll} \text{NaCN consumed in leaching} = 2\ 43 \times 2{,}000 & = & 4{,}860 \text{ lb} \\ \text{NaCN left in solution} = 0\ 68 \times 6{,}800 & = & \underline{4{,}620} \\ \hfill \text{Total NaCN at start} & = & 9{,}480 \text{ lb.} \end{array}$$

$$\text{Weight of solution: } \frac{9{,}480}{0.0025} = 3{,}792{,}000 \text{ lb.} = 1{,}896 \text{ tons}$$

6,800 − 1,896 = 4,904 tons of wash water used (2)

From Elsner's equation, 216 Ag requires 4 × 49 NaCN Then 21,350 oz. of Ag requires $^{196}/_{216} \times 21{,}350 = 19{,}370$ oz. of NaCN (ounces troy)

$$\frac{19{,}370}{14.58} = 1{,}330 \text{ lb. of NaCN actually used in dissolving silver.}$$

$$\frac{1{,}330}{4{,}860} = 27.4 \text{ per cent of NaCN consumed,}$$

or

$$\frac{1{,}330}{9{,}480} = 14.0 \text{ per cent of total NaCN used (3).}$$

Zn used in precipitating silver = $(^{65}/_{108} \times 20{,}330) \div 14.58 = 840$ lb.
Zn consumed = 1.34 × 2,000 = 2,680 lb.

$$\frac{840}{2{,}680} = 31.3 \text{ per cent (4).}$$

In problems on leaching the distinction between "extraction" and "recovery" should be noted. Extraction refers to the amount dissolved from the ore. Recovery refers to the amount obtained after precipitation from the solution.

Assay values are commonly stated in ounces per ton. These are ounces troy in a ton of 2,000 lb. avoirdupois. Since 29,166 oz. troy = 1 ton, 14.583 oz. troy = 1 lb. avoirdupois. Gold assays are often given in dollars per ton, which may be converted to ounces on the basis of $35 per troy ounce.

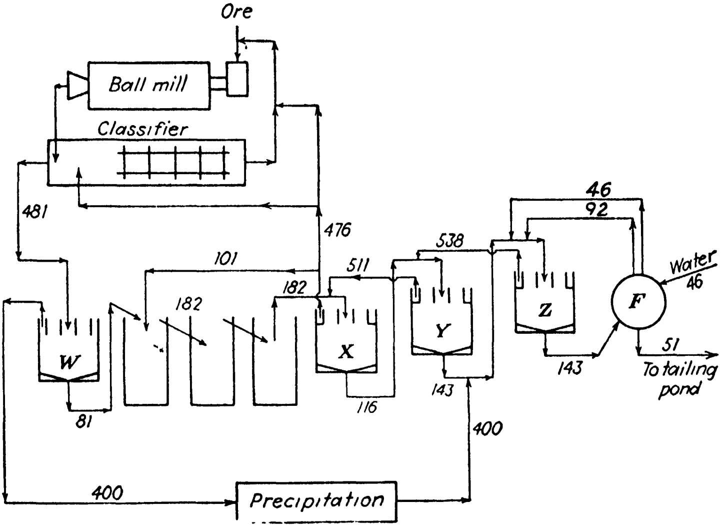

Fig. 11.—Flow sheet of C.C.D. cyanide plant (Example 38).

Continuous Countercurrent Decantation.—Of the several methods and types of apparatus used in carrying out leaching operations, continuous countercurrent decantation (C.C.D.) is one widely applied in cyanidation. It was first made possible by the invention of the Dorr thickener. As shown in the flow sheet (Fig. 11) the ore and cyanide solution pass together through the grinding circuit and then through a series of thickeners and agitators. Dissolving of gold (or silver) takes place in various parts of the circuit, but chiefly during grinding and agitation. A large part of the solution is withdrawn from the first thickener for precipitation; after precipitation the barren solution is returned to the circuit in one of the later thickeners. The flow sheet may be varied by the point of return, the strength of solution, the amount of solution going to precipitation, the ratio of solution to solids in the thickener discharges, etc.; all these are adjusted for a particular ore to obtain the maximum extraction with lowest loss of metal and cyanide.

The solution of a problem of this type depends on the fact that the amount of material leaving any unit of the system is equal to the amount entering; this is true with respect to the total weight of solution, the weight of gold, and the weight of NaCN. Equations based on these relations may be set up and solved to obtain the desired unknowns.

It is desirable first to draw the flow sheet in outline, after which the it may be "balanced" by determining the weights of solution in each line of flow according to the conditions of the problem, these weights then being entered in the flow diagram as has been done in Fig. 11. Equations are then formulated for determination of the assay values of the solutions at any desired points in the circuit. From the gold assay values the percentage of recovery can be calculated, and from the cyanide strengths the loss of NaCN can be obtained. Study of the following example[1] should make the procedure clear:

Example 38

A cyanide mill treats 100 tons of ore (wet) per day, using a C.C.D. flow sheet consisting of grinding circuit, first thickener, three agitators, three additional thickeners, and filter. The ore contains 5 per cent moisture. 400 tons of solution from the first thickener is precipitated to $0.02 per ton, the barren solution reentering the circuit in the fourth thickener The discharge from the first thickener is 54 per cent solids, those from the ensuing thickeners 45, 40, and 40 per cent solids. The agitators have 1.92 tons of solution per ton of ore The filter cake is 35 per cent moisture, and the displacement efficiency of the filter is 70 per cent (*i.e.*, 70 per cent of the value of the solution in the filter cake is recovered by washing). The total water added to the system (including moisture in ore and water added in the filter) is equal to the weight of solution going to the tailing pond in the cake There is dissolved from the ore $12 in gold per dry ton, 50 per cent being dissolved in the grinding circuit, 2 per cent in the first thickener, 45 per cent in the agitators, and 1 per cent in each of the other thickeners. The solution in the first thickener carries 2 lb. of NaCN per ton.

Required: 1. Balance the flow sheet with respect to the tons of solution in each flow line.

2. The assay values of the solution leaving each thickener and the filter.

3 The percentage of the dissolved values saved.

4. The cyanide strength of the solution leaving each thickener and the filter.

5. The mechanical loss of cyanide per ton of ore, cyanide consumption in the system being neglected.

Solution: The solution discharge from the first thickener will be the 400 tons for precipitation plus $^{46}/_{54} \times 95 = 81$ tons.

The solution in the agitators is $1.92 \times 95 = 182$ tons.

The discharge from the second thickener is $^{55}/_{45} \times 95 = 116$ tons, that from each of the last two, $^{60}/_{40} \times 95 = 143$ tons

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[1] Adapted from DORR, JOHN V N., "Cyanidation and Concentration of Gold and Silver Ores," p. 134, McGraw-Hill Book Company, Inc., New York, 1936. The data for this example and for Probs. 301–303 were supplied by E. A. Peretti.

The weight of the filter cake is $\frac{95}{0.65} = 146$ tons, and solution in it is $0.35 \times 146 = 51$ tons (to tailing pond). The wash water added to the filter is $51 - 5$ (in ore) $= 46$ tons. The solution return from the filter to the last thickener is $143 + 46 - 51 = 138$ tons (of which 51 tons is subject to the 70 per cent recovery).

The solution flow from the fourth to the third thickener is $400 + 143 + 138 - 143 = 538$ tons; from the third to the second, $538 + 116 - 143 = 511$ tons.

The solution return from the second thickener to the agitators is $182 - 81 = 101$ tons, and from this thickener to the grinding circuit $511 + 182 - 116 - 101 = 476$ tons. Solution leaving grinding circuit $= 476 + 5$ (in ore) $= 481$ tons

(In this example the grinding circuit is taken as a single unit, but in Fig. 11 it has been divided, as may be necessary in some problems.)

Let W, X, Y, Z, and F be the assay values in dollars per ton of the solution leaving the four thickeners and the filter, respectively. The following equations result from the gold contents of the solutions leaving and entering each unit:

$$\begin{aligned}
400W + 81W &= 476X + 0.52 \times \$12 \times 95 \\
116X + 476X &= 81W + 511Y + 0.46 \times \$12 \times 95 \\
143Y + 511Y &= 116X + 538Z + 0.01 \times \$12 \times 95. \\
143Z + 538Z &= 143Y + 92Z + 51(0.7)Z + 0.01 \times \$12 \times 95 + 400 \times \$0.02.
\end{aligned}$$

$$51F + 92Z + 51(0.7)Z = 143Z.$$

Solving these, we obtain $W = \$2.843$, $X = \$1.624$, $Y = \$0.403$, $Z = \$0.119$, $F = \$0.0357$ (2).

$$\text{Percentage of dissolved values lost} = \frac{51 \times \$0.0357}{95 \times \$12.00} = 0.160 \text{ per cent.}$$

$$\text{Percentage of dissolved values saved} = 99.840 \text{ per cent (3).}$$

Let w, x, y, z, and f be the cyanide strengths in pounds per ton of the solution leaving the four thickeners and the filter, respectively. The following equations result from the cyanide contents of the solutions leaving and entering each unit:

$$\begin{aligned}
w &= 2. \\
116x + 476x &= 81w + 511y. \\
143y + 511y &= 116x + 538z. \\
143z + 538z &= 143y + 400w + 92z + 51(0.7)z. \\
51f + 92z + 51(0.7)z &= 143z.
\end{aligned}$$

Therefore, $w = 2.000$, $x = 1.970$, $y = 1.957$, $z = 1.953$, $f = 0.585$ (4).

$$\text{Loss of cyanide} = \frac{51 \times 0.585}{100} = 0.298 \text{ lb. per ton of ore (5)}$$

When it is required to balance the grinding circuit, consisting of ball mill and classifier, it is necessary to know the circulating load. As used here, the circulating load is the ratio of the tonnage of sands returned to the mill to the tons of original feed.

In the plant the amounts of solids contained in the discharges of various units are usually obtained in terms of pulp densities. From these it is necessary to compute the percentage of solids in the discharge, or the water-solid ratio (parts water per part solids by weight). If S is the specific gravity of the dry ore, D is the water-solid ratio, and d is the pulp density, then:

$$d = \frac{\text{total weight of pulp}}{\text{total volume of pulp}} = \frac{D + 1}{D + \frac{1}{S}},$$

whence

$$D = \frac{S - d}{S(d - 1)}.$$

Problems

297. At the leaching plant of the New Cornelia Copper Company, Ajo, Ariz., a tank received a charge of 5,000 short tons of oxide ore carrying 1.57 per cent Cu. This was leached for 8 days with an H_2SO_4 solution, during which time there was dissolved per ton of ore leached 27 93 lb. of Cu, 6.8 of Fe, 7.33 of Al_2O_3, 3.31 of MgO. The tailings carried 0.18 per cent Cu.

The leaching solution at the end of 8 days had increased its average copper content by 0.66 per cent copper, and in addition one-tenth of the copper dissolved from the ore was contained in wash-water solution.

Per ton of ore leached there was discarded 254 lb. of the weakest wash-water solution, containing 0 38 per cent Cu and 0.10 per cent H_2SO_4, while 220 lb. of solution of the same composition remained entrained with the tailings Before discarding the above solution, it was passed over scrap iron, which freed it of Cu and H_2SO_4

The enriched leaching solution, together with some of the wash water, passed to electrolytic tanks, which deposited pure copper from it at a current efficiency of 71 per cent; the solution entered these tanks carrying 3.06 per cent copper and left with 2 62 per cent copper. There were 152 tanks

Required: 1. The percentage extraction of copper from the ore

2. The tons of tailings.

3. The tons of leaching solution, exclusive of wash water, neglecting gain or loss during leaching

4. The indicated consumption of H_2SO_4, expressed in pounds per pound of copper dissolved, disregarding the regeneration of H_2SO_4 during electrodeposition.

5. The percentage of the copper in the ore which is·

a. Undissolved in the tailings

b. Lost in solution entrained with the tailings.

c. Recovered as cement copper

d. By difference, recovered as electrolytic copper.

6. The percentage of the indicated consumption of H_2SO_4 that is regenerated during electrodeposition.

7. The pounds of scrap iron consumed, expressed in pounds per pound of copper dissolved from the ore.

8. Total tons of solution (including wash water) passing to the electrolytic tanks.

9. The amperes required in each tank.

298. An electrolytic zinc plant operates six circuits of tanks with 144 tanks per circuit; each circuit is divided into 24 circulation cascades. The crude leach solution carries 110 g. of Zn per liter, 1.7 g. of Cu, 0.2 g. of Cd, and a small amount of H_2SO_4. The Cu and Cd in the leach solution are precipitated, and the free acid is neutralized by adding zinc dust made by atomizing melted zinc from a preceding charge; 8 per cent of the zinc made is required as zinc dust. The overflow from the electrolytic tanks carries 30 g. of zinc per liter. Current density, 30 amp. per square foot; 28 lead anodes and 27 aluminum cathodes, per tank; cathodes are pulled every 48 hr.; cathode dimensions, 2 by 3 ft. The voltage of the tank varies from 4.0 volts at the start to 3.6 at the end of the deposition. Current efficiency, 88 per cent.

Required: 1. The pounds of zinc made per day.

2. The average voltage, per circuit.

3. The kilowatt-hours used, per pound of zinc.

4. The weight of the cathode slab that is removed from each side of the cathode.

5. The voltage absorbed as reaction potential.

6. The heat generated by the electrolysis, per tank.

7. The rate of circulation of solution through each cascade.

8. The amount of copper and cadmium removed from the entire solution daily

9. The H_2SO_4 content of (*a*) the crude leach solution and (*b*) the tank overflow

299. *A* is a copper ore, *B* a silver ore, and *C* a gold ore. Each contains the valuable metal to the amount of $5 per ton of 2,000 lb. Assume that each ore weighs 125 lb. per cubic foot of space occupied.

Assume the value of copper as $0.12½ per lb., silver as $0.35 per ounce, and gold as $35 per ounce.

Required: 1. The weight in kilograms of the valuable metal in each ore, and the percentage content by weight.

2. The volume in cubic centimeters occupied by the valuable metal in each ore, and the percentage content by volume.

3. Commercial gold leaf is commonly $\frac{1}{200,000}$ in. in thickness Calculate the value of gold in a flake of this leaf having an area of 1 sq mm., and the number of such flakes required to equal the value of gold in a ton of ore *C*.

4. What would be the area in square feet of a sheet of this gold leaf containing $5 worth of gold?

5. What would be the value of gold in a ton of ore containing one of these flakes in each cubic section of 3 by 3 by 3 in ?

300. The mill of the Mexico Mines, El Oro, Mexico, treated ore averaging $12 gold and 7 oz. silver per ton. This was cyanided by the all-sliming process, 80 tons (dry weight) per charge being treated. The tailings after agitation carried 60 cts. gold and 1.3 oz. of silver per ton. A charge yielded 400 tons of solution for the precipitation tanks.

The solution used for agitation was 0.05 per cent KCN. The total consumption of KCN was 120 lb. per charge. The total consumption of zinc was 88 lb. per charge

Required: 1. The percentages of gold and of silver in the ore.

2. The percentage extraction of gold and of silver.

3. The assay of the solution entering the precipitation boxes (gold in dollars and silver in ounces, per ton).

4. The percentage of the KCN consumption that was actually used in dissolving gold and silver.

5. The percentage of the zinc consumption that was actually used in precipitating gold and silver

301. A cyanide mill treats 120 tons of gold ore per day, dissolving $14 per dry ton. The ore carries 10 per cent moisture. Assume the same flow sheet and other data as in Example 38, except for the following changes:

300 tons of solution goes to precipitation; the return barren solution reenters the circuit in the third thickener: and the ratio of solution to ore in the agitators is 2.0:1.

Required: The same as in Example 38.

302. In a cyanide plant using the C.C.D. system according to the flow sheet shown in Fig. 11, the following data are known:

150 tons of ore containing 10 per cent moisture is ground per day in the cyanide solution.

0.5 oz. of gold is dissolved per ton of dry ore; of this, 25 per cent is dissolved in the milling circuit, 69 per cent in the agitators, 2 per cent in each of the first two thickeners, and 1 per cent in each of the last two thickeners.

The densities of the various products are as follows: dry ore, 2.8; ball-mill discharge, 1.502; classifier overflow, 1.201; classifier sands, 2.006; discharges of all thickeners, 1.407; filter cake, 1.777; pulp in agitators, 1.29.

The classifier circulating load is 120 per cent.

The barren solution assays 0.002 oz per ton.

The displacement efficiency of the filter is 65 per cent

Just enough wash water is added to balance the circuit.

Required: 1. Balance the flow sheet for solution tonnages.

2. The gold assay of the solution leaving each thickener and the filter, in ounces per ton.

3. The percentage loss of dissolved gold.

303. The flow sheet of a C C.D. cyanide plant consists of a grinding circuit (with ball mill and classifier), thickener *A*, four agitators, thickeners *B* and *C*, and filter *F*. The operating data are as follows:

Ore ground per day, 130 tons, containing 10 per cent moisture and 0.45 oz. of gold per dry ton. Assume all gold dissolved and complete precipitation. 15 per cent of the gold is dissolved in the grinding mill, 81 per cent in the agitators, 2 per cent in thickener *A*, and 1 per cent in each of thickeners *B* and *C*. The specific gravity of the ore is 3 0; pulp density in the ball-mill discharge 1.435 and in the classifier overflow 1.154. There are 75 per cent solids in the classifier sands, 45 per cent solids in the discharge of *A*, 53 per cent in the discharge of *B*, and 62 per cent in the discharge of *C*. The circulating load through the classifiers is 60 per cent The agitation time is 28 hr. with a pulp having 33⅓ per cent solids. The displacement efficiency of the filter is 64 per cent. The filter cake contains 35 per cent moisture

Required: 1. Balance the flow sheet for solution tonnages.

2. The gold assays, in ounces per ton, of the solutions leaving *A*, *B*, *C*, and *F*, and the loss of dissolved values.

3. If the agitation time is found to be insufficient and is to be increased to 35 hr. without adding more agitators, to what figure will the daily tonnage have to be adjusted?

CHAPTER XVIII

METALLURGY OF ALUMINUM AND MAGNESIUM

The electrolysis of fused-salt baths is of great importance because it is the most practicable method for production of the chemically strong metals, in general all those metals occurring above manganese in the electropotential series. All our aluminum is obtained by this method and most of our magnesium. Recently other methods have been developed for magnesium and beryllium, and some of the rarer metals are sometimes obtained by reduction with a chemically stronger element.

Since the metals will be reduced, whether by electrolysis or otherwise, in the order of their chemical strength and since it is not possible to refine the chemically strong metals by the usual methods of oxidation or electrolysis of an aqueous solution, it becomes necessary to purify the salts of these metals before reduction. In the case of alumina this is usually done by the Bayer process. Some use has also been made of an electric-furnace method in which the impurities are reduced and removed as a ferroalloy while the purified Al_2O_3 remains unreduced (see Prob. 305, page 292).

The electrolysis of fused salts is governed by the same laws as the electrolysis of aqueous solutions, and similar methods of calculation are applicable. Faraday's laws are fundamental with respect to the current relations. Current efficiencies are relatively low, especially because of loss of metal as metal fog. Cell voltages have the same components as those discussed in Chap. XVI. The voltage of conduction through the electrolyte is usually not readily determined because of irregularity in the dimensional setup. Although conductivities of the fused salts are in general better than those of aqueous solutions, conduction voltages (*IR* drops) are high because of high current densities and long paths of current flow. Gas voltages are usually high, especially in view of the high current densities employed. Reaction voltages are also high because of the metals being chemically strong.

In calculating the reaction voltage for a fused salt, it is better to calculate the heat of the reaction ΔH at the actual cell temperature, instead of at room temperature (see Chap. V). Usually, however, the difference is small, and often the readily obtained value for ΔH at room temperature is a sufficiently close approximation. A problem will be given illustrating the difference involved in the case of the Hall-Heroult process for aluminum. The error occasioned by using ΔH at room temperature instead of at the cell temperature is less than that caused by using ΔH instead of ΔF, as should be done whenever ΔF can be obtained. In the aluminum cell the reaction voltage as calculated from ΔH for the reaction $Al_2O_3 = 2Al + \frac{3}{2}O_2$ at 1000°C. is 2.8, but it may be less than 2.0 after crediting the heat of formation of CO and CO_2 and from actual cell measurements appears to be about 1.7.

It has been debatable how much the reaction voltage of the aluminum cell is affected by the oxidation of the carbon anode. The question at issue is whether the energy of formation of the CO and CO_2 appears entirely as heat or is converted partly into electrical energy. The question cannot be answered here, but problems will be given in which the possible magnitude of the effect on the reaction voltage is calculated.

Energy Efficiency.—In fused-salt electrolysis it is often desired to know the energy efficiency of the cell as well as the current efficiency. If a "voltage efficiency" be regarded as the reaction voltage divided by the total cell voltage, then this multiplied by the current efficiency gives an approximation of the energy efficiency. However, the heat content of the molten metal at the cell temperature should be included as part of the useful heat, and this makes it desirable to calculate the energy efficiency in terms of Calories; the numerator is the heat of the reaction plus the heat content of the metal, while the denominator is the power input expressed in Calories. Some writers would include as useful heat the heat content of *all* the products of the reaction, but it seems better to regard the heat contained in gaseous products as waste heat, just as in a fuel-fired furnace.

Additional problems on aluminum and magnesium are given later (see Probs. 360, 383, and 397). In the electrothermic process of magnesium production, vapor pressure is an important factor; accordingly, problems on this process are included in Chap. XXIII, Vapor Pressure and Temperature-Pressure Relations in Chemical Reactions.

Problems

304. Pure alumina for aluminum production is produced by the Bayer process, using bauxite of the following composition:

	Per Cent
Al_2O_3	58
Fe_2O_3	6
SiO_2	4
TiO_2	2
H_2O	30

The ore is dried, ground, and digested with NaOH, forming a solution of $NaAlO_2$. The red mud filtered from this solution carries 26 per cent Al_2O_3, 21Fe_2O_3, and 14Na_2O; assume that it contains all the Fe_2O_3 and SiO_2 that were in the bauxite and that the SiO_2 is present in the form of the insoluble compound $Al_2O_3.Na_2O.3SiO_2.9H_2O$.

It is desired to have the filtered solution contain 1.5 mols of Na_2O to 1 mol of Al_2O_3.

Required: 1. The weight of red mud made for each 1,000 kg. of original bauxite.

2. The weight of Al_2O_3 lost in the insoluble compound, per kilogram of SiO_2, and the percentage this represents of the Al_2O_3 content of the bauxite.

3. The total loss of Al_2O_3 in the red mud, and its percentage of the Al_2O_3 content of the bauxite.

4. The weight of NaOH used in forming the insoluble compound, per kilogram of SiO_2, and the total loss of NaOH represented by the Na_2O in the red mud.

5. The weight of NaOH used in the process, per 1,000 kg. of bauxite, and the percentage of it lost in the red mud.

6. The heat of the reaction forming $NaAlO_2$, in Calories per kilogram-mol and in kilojoules per gram-mol.

305. A bauxite contained, after calcining, the following:

	Per Cent
Al_2O_3	85
Fe_2O_3	5
SiO_2	6
TiO_2	4

It is mixed with 10 per cent more carbon than necessary theoretically to reduce the impurities and is melted in an electric furnace. Assume that one-fourth of the excess carbon reduces Al_2O_3 to Al and the remainder dissolves in the metal.

The temperature of the molten alumina and of the escaping CO is 2100°C. and of the metal 1900°C.

Required: 1. The weight of carbon to be used, per 2,000 lb. of bauxite.

2. The percentage composition of the resulting alloy.

3. The kilowatt-hours necessary for 2,000 lb. of bauxite, at 75 per cent electrothermal efficiency.

4. Compare the value of the pure alumina at $0.02 per pound and of the alloy at $40 per ton with the cost of the power at $0.01 per kilowatt-hour.

306. An aluminum plant runs six series of cells with 70 cells in each series. Each series takes 20,000 amp. and 500 volts. Each furnace produces 300 lb of metal per day. The inside dimensions of the carbon lining of the bath are 8 by 4 by 1 ft.

Required: 1. The current efficiency.

2. The energy (in kilowatt-hours) required, per pound of metal made.

3. The current density at the cathode, assuming the sides of the cell inactive.

4. The annual capacity of the plant.

307. An aluminum plant has five series of cells with 60 cells in each series. Each series takes 28,000 amp. and 450 volts. The current efficiency is 88 per cent.

Required: 1. The annual capacity of the plant, in pounds.

2. The kilowatt-hours consumed, per pound of metal made.

3. The voltage absorbed by the chemical reaction, assuming that one-third of the oxygen from Al_2O_3 goes to CO, two-thirds to CO_2. (Calculate for room temperature.)

4. The rate of heat production in the cell, in Calories per minute.

5. The total volume of gases liberated in each cell in 24 hr.

308. The output of an aluminum plant is 35,000 kg. per day. It uses 37,500 kw., the individual cells taking 7 volts and the current passing through each being 15,000 amp. Assume that the reduction of the alumina is according to the equation

$$2Al_2O_3 + 5C = 4CO + CO_2 + 4Al.$$

The aluminum is tapped from the cells at 900°C.

Required: 1. The number of cells operating.

2. The ampere efficiency of producing the aluminum.

3. The energy efficiency at which the cells utilize the energy of the current, counting the useful work done as the reduction of the alumina and the supplying of the heat taken by the molten metal.

309. In the Hall bath, Al_2O_3 is dissolved and practically takes the liquid form at 1000°C. It is electrolyzed at 1000°C. to Al and a mixture of 50 per cent CO and 50 per cent CO_2.

Each cell takes 15,000 amp. at 6.5 volts. The lower surface is melted Al, area 150 by 250 cm. The anodes work at an average distance of 3 cm. from the cathode surface.

The plant uses 40,000 kw.

Required: 1. The output of the plant per day, taking the current efficiency at 80 per cent.

2. The theoretical voltage for complete decomposition of Al_2O_3, liquid at 1000°C., into 2 Al and 3 O, each at 1000°C.

3. The theoretical voltage corresponding to burning of carbon at 1000°C. by oxygen at 1000° to the mixture of CO_2 and CO given, also at 1000°C.

4. The reaction voltage that will be required in the ordinary running of the cell, crediting generation of voltage as in 3.

5. The resistivity of the electrolyte. (Allow 0.6 volt for gas voltage and contacts Assume that the average cross-sectional area for current flow is 10 per cent less than the area of the cathode surface.)

310. An aluminum plant has 800 cells, each taking 20,000 amp at 6 8 volts The output of the plant is 240,000 lb. of aluminum per day The gases escaping from the pots analyze 40 per cent CO and 60 per cent CO_2.

The reduction takes place at 1000°C.; the Al_2O_3 dissolved in cryolite is practically in the liquid state at this temperature.

Required: 1. The ampere efficiency of deposition.

2. The chemical reaction expressing the reduction of Al_2O_3 and consumption of the electrodes.

3 The voltage of the reaction, as calculated according to Thomson's rule from the reaction beginning and ending at 1000°C., (*a*) assuming that the electrochemical action is simply decomposition of Al_2O_3, the formation of CO and CO_2 being a secondary chemical effect; (*b*) assuming that the entire reaction takes place electrochemically.

4. The energy efficiency at which the cells utilize their power input.

311. The electrolysis in a cell producing magnesium by the chloride process is expressed in the reaction

$$MgCl_2 = Mg + Cl_2.$$

The reaction takes place at 700°C.

A plant using this process has 140 cells in series; each cell receives 14,000 amp. at 8 volts. The current efficiency is 75 per cent.

Required: 1. The heat of the reaction at 700°C.

2. The reaction voltage as calculated from Thomson's rule, at 700°C.

3. The output of the plant in 24 hr.

4. The energy efficiency, counting the heat in the metal at 700° as useful heat, but disregarding heat in the gases.

5. The kilowatt-hours consumed per pound of magnesium

312. An electrolytic cell for magnesium (oxide process) is a ¾-in. steel jacket, 5 by 7 ft. and 4 ft. high (outside dimensions), lined with a layer of solid electrolyte 1 ft. thick, cooled by water pipes. The bath consists of 45 per cent MgF_2, 45 BaF_2, 10 NaF and is run at a temperature of 950°C. MgO is dissolved in this bath to the extent of 0.3 per cent. The output of the cell is 200 lb. daily of metal of a composition Mg, 98 per cent; Na, 1; bath salts, 1. Current, 14,000 amp.; voltage, 13. Specific gravity of MgF_2, 2.5; of BaF_2, 4.8; of NaF, 2.7.

Required: 1. The total weight of electrolyte in the cell.

2. The weight of liquid electrolyte, and the amount of MgO in solution in it. (Neglect any frozen electrolyte on top surface, and assume specific gravity of liquid salts the same as for solid.)

3. The weight of all materials to be added to the bath daily, to maintain it unchanged.

4. The current efficiency of the cell.

5. The voltage theoretically required for electrolyte decomposition.

6. The kilowatt-hours used per pound of magnesium.

7. The energy efficiency of the cell.

CHAPTER XIX

VOLATILIZATION OF METALS IN MELTING

The tendency of a substance to volatilize at any given temperature is measured by its vapor pressure at that temperature. The normal boiling point is the temperature at which the vapor pressure equals 760 mm. If the surrounding pressure is below 760 mm., the substance will boil at a temperature below its normal point; *i.e.*, the actual boiling point is lowered below normal by a decrease in surrounding pressure because the substance boils when its vapor pressure equals or exceeds the total opposing pressure.

At the boiling point the metal vaporizes freely so long as the vapor formed is permitted to escape so that the opposing pressure is not built up.

But the metal will also vaporize below the boiling point, since it exerts a vapor pressure at all temperatures, and will continue to vaporize so long as the vapor formed escapes so that the pressure *of the metal vapor* in contact with the metal remains below the vapor pressure of the metal.

If the vapor does not escape but remains immediately above the body of metal, a condition of equilibrium is soon established and no more vapor is formed; or, more precisely, the amount of vapor forming is exactly equal to the amount condensing, since these two processes are undoubtedly going on to some extent continuously; at equilibrium they exactly balance, and there is no *net* vaporization or net condensation. The metal will vaporize from the solid state as well as from the molten, but the amount of vaporization then is much smaller because the temperature is lower.

The terms "vaporize" and "volatilize" may be used interchangeably.

When heat is supplied to molten metal below the boiling point, nearly all the heat absorbed by the metal goes to raise its temperature. But since some volatilization is going on, a small part of the heat absorbed enters the vapor formed as latent heat of vaporization. Once the boiling point is reached, the temperature stops rising (assuming that the metal is in an open container so that the surrounding pressure remains constant), and now all the heat absorbed by the metal is used in vaporization. The rate of vaporization—*i.e.*, the amount of metal vaporized per unit of time—is then determined by the rate of absorption of heat.

The maximum amount of metal that can be volatilized in a furnace at a given temperature can readily be calculated (by application of Dalton's law) from the maximum vapor pressure and the volume of gas passing through the furnace. But the partial pressure of the metal vapor in the gases leaving the furnace may be anything less than the maximum vapor pressure of the metal; the gases will seldom if ever be saturated with the metal. Calculation of the actual amount of metal vaporized requires knowledge of the percentage of saturation. Nevertheless, a calculation without knowing the percentage saturation may often be useful. It may be desired to know the maximum possible loss of metal as vapor, or it may be possible to assume a probable percentage of saturation and thus arrive at an estimate of the volatilization loss.

The vapor pressures of some metals are high enough at their melting points to cause an appreciable loss in melting, especially if the molten bath is superheated too far above the melting point. Excessive loss may occur in this manner, for example, in melting silver, gold, and metals of the platinum group. Many other metals have wholly negligible vapor pressures at their melting points and some distance above; but if superheated greatly, as they may be in a blast furnace or an electric furnace, a large amount of vaporization occurs. Vaporization of manganese, silicon, and other elements is often encountered in electric furnaces. Loss of both lead and silver is important in the lead blast furnace and would be much higher if the top of the furnace were not kept relatively cool. Not all the loss of metal in blast-furnace fume can be ascribed to vaporization of metal as such, since many compounds of the metals volatilize more easily than the metals themselves. This is generally true in furnace work and is sometimes taken advantage of in the design of "volatilization processes" for extraction of metals from their ores.

Chemical and metallurgical literature contains many statements like the following: "Copper begins to volatilize at 1200°C." It is evident that such statements have no meaning, since metals volatilize at any temperature, the amount increasing with the temperature along an unbroken curve up to the melting point and then along another unbroken curve up to the boiling point. If it is desired to compare the volatilities of different metals on the basis of temperature, at temperatures far below the boiling points, a table could easily be computed with a fair degree of precision, giving the temperatures at which each metal has a vapor pressure of any figure adopted as a standard for the table, say 0.01 mm. Following are the temperatures at which five of the common metals have a vapor pressure of 0.01 mm.:

	Degrees Centigrade
Zinc	350
Lead	700
Silver	1020
Copper	1260
Iron	1470

It is interesting to note that of these five temperatures those for zinc and iron are below the melting points of those metals, while those for lead, silver, and copper are above their melting points.

The vapor pressures of a few of the more volatile metals have been measured over limited ranges of temperatures, and these observed values may be obtained from reference tables for use in calculation. These available data are so limited, however, that it is generally desirable to use another method of obtaining the vapor pressures of metals. This method is discussed at length in Chap. XXIII. The theory of the method will be taken for granted in the present chapter, and merely its use for finding the vapor pressures of metals will be indicated. It should be noted here that, while the method is in reality an approximation, it is sufficiently close for practical purposes in almost any case.

In order to find the vapor pressure of an element at a given temperature by this method, the temperature (expressed in degrees Kelvin) is substituted for T in an equation of the form

$$\log p = -\frac{A}{T} + B,$$

where A and B are constants for a given metal. The values of these constants are given in Table XXII, page 399, for the different elements. It will be noted from the table that the values to be used for these constants are different when the metals are below their freezing points; the table gives both sets of values. The figures given in the table are in such units that p, the vapor pressure, is obtained in millimeters of mercury.

At the melting point it is immaterial whether the constants for the solid metal or for the liquid metal are used; both give the same result, the metal being partly solid and partly liquid during melting.

Dalton's Law of Partial Pressures.—The ratio of p to the total pressure is the same as the ratio of the volume of the vapor to the total volume of gas. Or the ratio of p to the pressure of any other gas or gases present is the same as the ratio of the volume of the vapor to the volume of the other gas or gases. This follows directly from Dalton's law of partial pressures, which may be stated as follows: **The pressure exerted by a mixture of gases is equal to the sum of the separate pressures which each gas would exert if it alone occupied the whole volume.** The principle is expressed in the following equation:

$$PV = V(p_1 + p_2 + p_3 + \cdots).$$

Calculation of the Volume of Metal Vapor in a Given Volume of Furnace Gases.—The vapor pressure of the metal having been obtained for the temperature given, this may, in accordance with the principle just stated, be substituted in the expression

$$\frac{p_1}{p_2} = \frac{V_1}{V_2}, \qquad \text{or} \qquad V_1 = \frac{p_1}{p_2} V_2,$$

in which V_1 is the volume of the metal vapor, p_1 is its vapor pressure, and p_2 is the total pressure when V_2 is the total volume of gases, or p_2 is the partial pressure of a volume of gas equal to V_2.

The application of this principle for determining the maximum amount of metal lost by volatilization in a melting furnace, for example, affords no difficulty when the volume of the gases passing through the furnace is known and when the temperature is constant. If the temperature varies, as, for example, during heating of the furnace, the problem becomes one of integrating the loss over a period between certain temperature limits. The necessary data for actual integration, however, will not ordinarily be available. It will in general be necessary to assume some average for the temperatures. This should be assumed considerably above the arithmetical mean of the initial and final temperatures for the period, since it is well known that furnaces heat more and more slowly as the temperature rises; as a result, the temperature will be in the upper part of the range for a longer time than in the lower part. If desired, greater accuracy can be obtained by dividing the heating period into several parts and calculating the loss of metal for each part separately from the average temperature during each part.

Finding the actual loss of metal instead of merely the maximum possible loss introduces the further uncertainty of assuming the percentage of saturation of the furnace gases.

The actual pressure of the metal vapor having been determined by multiplying its maximum vapor pressure by the percentage saturation, the temperature at which this vapor will saturate the gas mixture may be found by again using the vapor-pressure formula

$$\log p = -\frac{A}{T} + B,$$

putting in the known value of p, and solving for T. Since p is the maximum or saturation pressure, cooling below the corresponding temperature causes the vapor to begin condensing to liquid.

Example 39

1,500 kg. of silver crystals is melted in an oil-fired furnace and brought to a temperature 150°C. above the melting point for casting into bars. The operation may be divided into three parts:

- *a*. Heating to melting point (961°C.).
- *b*. Melting.
- *c*. Superheating.

The thermal efficiency of the furnace during these periods is 13, 10, and 8 per cent, respectively. The fuel oil is burned at a constant rate of 1 kg. per minute, using air 20 per cent in excess of the theoretical amount. The analysis of the oil is:

	Per Cent
C	85.1
H	12.3
S	1.7
O	0.5
N	0.4

Assume the gases 25 per cent saturated with silver vapor. Assume that the average temperature during the heating and superheating is 50 per cent above the arithmetical mean.

Required: 1. The time of each period, and the volume of furnace gases passing in each period.

2. The loss of silver by volatilization in each period, in grams.

3. With a number of furnaces working at the same time, on different stages, what would be the average silver content of the furnace gases, in grams per cubic meter?

4. At what temperature will silver begin to condense from the average gas?

5. At what temperature will the condensation of the silver be 99.9 per cent complete?

Solution: The calorific power of the fuel is first calculated and found to be 10,470 Cal. per kilogram, which is the heat supplied per minute. The heat required in each of the three periods is as follows:

(*a*) $$\frac{1{,}500 \times 59.7}{0.13} = 689{,}000 \text{ Cal.}$$

(*b*) $$\frac{1{,}500 \times 25.0}{0.10} = 375{,}000$$

(*c*) $$\frac{1{,}500 \times 0.086 \times 150}{0.08} = 242{,}000$$

The time of each period is then:

(*a*) $689{,}000 \div 10{,}470 = 65.8$ min.

(*b*) $375{,}000 \div 10{,}470 = 35.8$

(*c*) $242{,}000 \div 10{,}470 = 23.1$

The volume of the products of combustion per kilogram of oil is now calculated and found to be 13.82 cu. m. Then the volume of gases passing through the furnace in each period is:

(*a*) $65.8 \times 13.82 = 910$ cu. m.

(*b*) $35.8 \times 13.82 = 495$

(*c*) $23.1 \times 13.82 = 319$ cu. m. (1).

The average temperature in each period is, according to the assumption:

(*a*) $\frac{961}{2} \times 1.5 = 721$°C. = 994°K.

(*b*) 961°C. = 1234°K.

(*c*) $961 + (75 \times 1.5) = 1074$°C. = 1347°K.

The metal is solid in the first period, partly solid and partly liquid in the second, and liquid in the third.

(*a*) $$\log p = -\frac{13{,}860}{994} + 8.704. \qquad p = 0.000006 \text{ mm.}$$

(*b*) $$\log p = -\frac{13{,}270}{1{,}234} + 8.225. \qquad p = 0.003$$

(*c*) $$\log p = -\frac{13{,}270}{1{,}347} + 8.225. \qquad p = 0.024$$

Since the gases are one-fourth saturated, the actual pressures of the silver vapor are one-fourth of these. Then the loss of silver in each period is as follows:

$$(a)\ \frac{0.0000015}{760 - 0.0000015} \times 910 = 0.000002 \text{ cu. m.} \times \frac{108}{22.4} \times 1{,}000 = 0.01 \text{ g}$$

$$(b)\ \frac{0.00075}{760 - 0.00075} \times 495 = 0.00049 \times \frac{108}{22.4} \times 1{,}000 = 2.4$$

$$(c)\ \frac{0.006}{760 - 0.006} \times 319 = 0.00252 \times \frac{108}{22.4} \times 1{,}000 = 12.1 \text{ g. (2).}$$

The average silver content of the gases will be the total weight of silver divided by the total volume of gas.

$$\frac{14.51}{1{,}724} = 0.0084 \text{ g. per cubic meter (3).}$$

$$0.0084 \times \frac{22.4}{108} = 0.0017 \text{ liter per cubic meter}$$

$$= 0.00017 \text{ per cent by volume}$$

The partial pressure of the silver vapor in the gas mixture is therefore 0.0000017 × 760 = 0.0013 mm. Substituting this for p in the formula:

$$\log 0.0013 = -\frac{13{,}860}{T} + 8.704.$$

$$T = 1196^\circ\text{K.} = 923^\circ\text{C (4)}$$

0.001 × 0.0017 = 0.0000017 liter of silver vapor remains per cubic meter (1,000 liters) of gas mixture when 99.9 per cent has condensed. Then $\frac{p}{760 - p} \times 1{,}000 = 0.0000017$, or $p = 0.00000129$ mm. Using this for p, $T = 951^\circ$K. = 678°C (5).

Problems

313. A charge of 200 metric tons of cathode copper is melted and cast in a wire-bar furnace. The volume of gases passing over it is 25,000 cu. m. per hour, measured at standard conditions. The time of the process is 23 hr., divided as follows.

a. Heating to the melting point (1084°C.), 4 hr.
b. Melting, at 1084°, 11 hr.
c. Superheating to 1300°, 2 hr.
d. Casting, at 1300°, 6 hr.

Assume the gases passing through the furnace to become 20 per cent saturated with metallic copper vapor. Assume the average temperature during a heating period to be 50 per cent above the arithmetical mean of the temperature during the period.

Required: The grams of copper vaporized in each of the four periods.

314. The gases issuing from a copper converter consist only of SO_2 and N_2. The volume of the gases during the slag-forming stage is 16,930 cu. m. and during the blister-forming stage 6,670 cu. m., both at standard conditions. Neglect any copper, iron, or sulphur in the flux.

The average temperature of the gases during the latter stage is 1200°C. The gases become one-third saturated with copper vapor.

Required. 1. The weight and grade of the matte.

2. The weight of copper volatilized in the blister-forming stage.

315. The ore smelted in a copper blast furnace amounts to 500 tons daily and carries 34 per cent FeS_2 together with 7 per cent Cu_3AsS_4. One atom of sulphur is expelled from the FeS_2 without oxidation, entering the gases as S_2 vapor. All the arsenic is oxidized and enters the gases as As_2O_3 vapor. The volume of gases leaving the furnace is 200,000 cu. ft. (standard conditions) per ton of ore smelted The gases leave the flue system at a temperature of 140°C.

Required: 1. The weight of As_2O_3 passing out of the furnace daily, in pounds.

2. The percentages of the S_2 and of the As_2O_3 contained in the gases that escape from the flues uncondensed at the temperature of 140°C

316. In a silver refinery the silver-melting furnaces burn 150 kg of oil per day, using 50 per cent excess air, and the gases pass over the silver at an average temperature of 1300°C. Assume that the gases become one-fourth saturated with silver vapor. The oil is 85 per cent C, 15 per cent H.

Required: 1. The weight of silver in the furnace gases, per day

2. The temperature at which the silver would begin to condense from the furnace gases as they cool in the flue, and the temperature at which three-fourths of the silver would have condensed.

3. The weight of silver in the furnace gases per day if the average temperature were 1050° instead of 1300°C.

317. Doré bullion 990 fine in silver, 3 5 fine in gold, is parted by the Moebius process. Pure silver is deposited at the cathode, while the gold is collected in a slime carrying 50 per cent Au and 5 per cent Ag.

The capacity of the plant is 161,000 oz. of cathode silver per day at a current efficiency of 90 per cent Each tank has four rows of Doré anodes and five copper cathodes each 20 in. wide and immersed to a depth of 15 in. The current density is 24 amp per square foot of active cathode surface. Each tank contains 4 cu. ft. of electrolyte, which carries 25 g. of silver per liter. The tanks are connected in series and the plates in parallel Anode scrap, 30 per cent

Value of gold $35 per ounce, silver $0.40 per ounce.

The cathode silver is melted in three charges daily in an oil-fired furnace for casting into bars. The furnace gases from each charge, amounting to 900 cu. m. (standard conditions), become one-fourth saturated with silver vapor at a temperature of 1077°C.

Required: 1. The number of tanks in the plant

2. The weight of gold and silver in process, and the daily interest charge thereon at the rate of 6 per cent per annum

3. The weight of silver in the slimes, per day.

4. The weight of silver in the melting furnace gases, per day

5. The temperature at which silver will begin to condense from the gases as they cool

318. Measurements taken on an oil-fired furnace melting fine gold show that the temperature at the exit to the flue is 1150°C. and the volume of flue gases 315 cu. m. (standard conditions) per hour. The gases are one-sixth saturated with gold, and the furnace is run at the above average temperature 3 hr. per day 300 days in the year.

Required: 1. The weight of gold that would pass into the flue in a year.

2. When the flue gases have cooled to a temperature low enough to start condensation of the gold vapor contained, what is the partial pressure of the gold vapor in millimeters, and what is the percentage by volume of gold vapor contained in them?

3. The temperature at which condensation would begin.

319. Gold bullion of the composition Au, 85 per cent; Ag, 10; Cu, 5 is melted down, cast into anodes, and refined by the Wohlwill process.

On melting, the average temperature of the surface of the metal is 1250°C. over a period of 2 hr. The volume of the gases escaping from the furnace is 7 cu. m. per minute (standard conditions). Assume that the gases become 10 per cent saturated with each of the three metals.

In refining, the current used is 400 amp. and the current efficiency of cathode deposition is 100 per cent. It is found necessary to add 7.8 kg. of $AuCl_3$ once in 24 hr. running, in order to keep up the gold content of the electrolyte.

Required: 1. The grams of gold, silver, and copper volatilized in melting.

2. The current efficiency of gold solution at the anode.

NOTE: To obtain the vapor pressure of each metal in the molten bullion, multiply the vapor pressure as calculated for the pure element by the atomic percentage in the bullion.

320. The charge of a lead blast furnace, weighing 250 tons, carries 5 per cent S and gives per ton of charge a matte fall of 150 kg containing 20 per cent S. Assume that the rest of the sulphur is in the gases as SO_2, the gases analyzing 0.6 per cent SO_2. Temperature of the gases leaving the smelting zone, 1400°C.; pressure, 800 mm.

Required: 1. The weight of lead carried out of the smelting zone as lead vapor, assuming the gases one-third saturated therewith, per ton of charge.

2. The percentage of this lead which has condensed when the gases have reached a point where the temperature is 750°C., pressure 780 mm., neglecting any effect of the formation of fume.

321. A lead blast furnace smelts per day 200 tons of charge carrying 15 per cent Pb. The coke used amounts to 13 per cent of the charge and carries 90 per cent carbon. Carbonates in the charge contain an additional amount of carbon equal to 1 per cent of the charge. The gases issuing from the top of the furnace analyze 22 per cent CO_2 and 10 per cent CO. At the tuyères (and smelting zone), assume that the blast burns the carbon entirely to CO and that 90 per cent of the carbon of the coke is so consumed.

The temperature of the gases leaving the top of the furnace is 400°C., and they are saturated with lead vapor. The temperature in the smelting zone is 1200°, assume that the gases here become one-fourth saturated with lead vapor. Pressure at top, 760 mm.; in smelting zone, 785 mm.

Required: 1. The weight of lead escaping from the furnace as vapor, per day.

2. The percentage of the total lead charged that is vaporized in the smelting zone.

3. At what temperature of the issuing gases would all the lead charged be lost as vapor?

CHAPTER XX

METALLURGY OF LEAD

Lead roasting may be carried out in shaft furnaces such as are used for copper ores, but more often blast roasting, usually with Dwight-Lloyd machines, is practiced. It has been the custom to leave a small amount of sulphur in the roasted ore, resulting in the formation of some matte in the blast furnace, which takes up most of the copper charged as Cu_2S. The matte will also contain FeS and PbS. In recent years it has become the practice in some plants to eliminate practically all the sulphur from the ore by roasting, with the result that no matte is formed in smelting. In this case all the copper contained in the charge will be found in the lead bullion. The lead bullion contains the bulk of the lead charged and also most of the precious metals. It usually analyzes 99+ per cent lead and in many types of calculation can be assumed to be pure lead.

Problems on lead roasting have been included in Chap. XIV, Roasting and Sintering. Some additional ones, including a heat-balance problem, are given at the end of the present chapter. A number of problems on the lead blast furnace are also given, including charge and heat balances and charge calculation. The solution of these should be readily understood after the principles involved in the iron and copper blast-furnace problems have been mastered. The lead-smelting problems are perhaps a little more complex; considerable time will be required for the solution of some of those given at the end of this chapter.

Boyd Dudley, Jr.,[1] has fully discussed and illustrated charge calculations for the lead blast furnace. H. O. Hofman[2] has given a detailed charge and heat balance of a lead blast furnace.

Besides blast-furnace smelting of lead, the ore-hearth process is used extensively. No new principles of calculation are involved, however. Two problems on the ore hearth are given to bring out certain features of the process.

The lead bullion obtained from the blast furnace must be refined and the precious metals extracted from it. Desilverization of the lead is most often done by the Parkes process, in which a small amount of zinc is added to the molten lead, the silver and gold uniting with the zinc and rising to the top of the kettle in a "zinc crust." Although it has been shown that this action is essentially the formation of a ternary alloy of silver, zinc, and lead, there is also formation of the compound Ag_2Zn_3, and calculations may be based in part on this fact. Conditions in the process are too variable, however, to permit of certainty in general calculation, and perhaps the chief value of the problems on desilverization, a number of which are stated at the end of this chapter, is the general view that they give of the relations in the process. No special discussion of these is necessary. It may be useful to point out that the assay of lead bullion is commonly stated in terms of troy ounces per ton of 2,000 lb. avoirdupois. There are 29,166 oz. troy in the ton—the basis of the assay-ton system of weights. Hence 1 lb. avoirdupois = 14.583 oz. troy.

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[1] See footnote, p. 184.

[2] "Metallurgy of Lead," pp. 345–351, McGraw-Hill Book Company, Inc., New York, 1918.

The Pattinson process of desilverization, though now of minor importance, is interesting in theory and affords an interesting calculation, as illustrated in Prob. 342.

The zinc crust obtained in the Parkes process is treated by distillation to remove the zinc from it, leaving a rich lead-silver-gold alloy that can be cupelled. Distillation of this crust introduces the question of simultaneous vaporization of different elements. Problems of this type are given and discussed in Chap. XXIII under the head of Vapor Pressure of Alloys.

The Betts electrolytic process affords another method of desilverizing lead, particularly applicable when the bullion is high in bismuth. Problems 283, 284, 343, and 344 deal with this process, which closely resembles electrolytic refining of copper in principle.

Problems

322. Lead concentrates are roasted in a Wedge mechanical furnace. They are composed of PbS, FeS_2, SiO_2, and moisture, and contain 31 per cent SiO_2, 11 S, 8 H_2O.

PbS is oxidized completely to PbO and SO_2. FeS_2 is oxidized to Fe_3O_4 and SO_2, except that enough FeS remains to contain 10 per cent of the weight of sulphur present in the raw concentrates. The gases contain 6 per cent SO_2.

Required: 1. The percentages of PbS, FeS_2, and SiO_2 in the concentrates (dry analysis).

2. The percentage composition of the roasted material.

3. The percentage of excess air used above that theoretically required for the roasting reactions.

4. The percentage composition of the gases.

323. Galena concentrates are composed of PbS, FeS_2, and SiO_2. The moist concentrates contain 8 per cent H_2O, 28 SiO_2, and 11 S. They are roasted down to 4 per cent S, the roasted ore being composed of FeS, PbS, and PbO and SiO_2, the last two combined as a silicate.

The furnace is fired with coal containing 72 per cent C, 4 H, 8 O, 3 H_2O, 13 ash.

The furnace gases (analyzed dry) are 3 per cent SO_2, 3.5 CO_2, 10.5 O_2. Neglect moisture in the air.

Required: Per ton of concentrates:

1. The weight of roasted ore.
2. The volume of the furnace gases, including moisture.
3. The weight of coal used.

324. In Prob. 323 the heat of formation of the lead silicate is 200 lb.-cal. per pound of SiO_2.

The furnace gases leave the furnace at 300°C. The roasted ore is discharged at 500°C. Assume the air and concentrates at 0°C. Neglect heat in the coal ashes

Required: A heat balance of the furnace.

325. Lead ore is roasted on a Dwight-Lloyd machine, which treats a charge containing 38 per cent SiO_2, 5 $CaCO_3$, 16 S as PbS and FeS_2, moistened with 10 per cent of its weight of water. The sinter produced carries 2 per cent S as FeS, the rest of the iron as FeO, 5 per cent of the lead as metallic Pb, and the remainder of the lead as PbO combined with the SiO_2.

The gases contain 8 per cent free oxygen. The ore layer is 5 in. deep An oil burner ignites the charge by heating a layer ⅛ in. deep to an average temperature of 500°C, using 3 kg. of oil per ton of dry charge. Composition of the oil, 85 per cent C and 15 per cent H. Assume that the oil is burned with the theoretical requirement of air and that only one-third of its products of combustion is drawn down through the ore bed

Required: 1. The thermal efficiency of the ignition.

2. The weight of the sinter, per ton of dry charge.
3. The volume of the gases, per ton of dry charge.

326. A concentrated lead ore contains 60 per cent PbS, 4 FeS_2, 3 Al_2O_3, 2 CaO, 31 SiO_2. It is first roasted, oxidizing all the FeS_2 and 90 per cent of the PbS. The roasted ore is then smelted in a blast furnace, using as flux enough Fe_2O_3 and $CaCO_3$ to make a slag having a SiO_2:FeO·CaO ratio of 35:50·15 and using coke equal to 16 per cent of the weight of the ore. The coke is 85 per cent C and 15 per cent SiO_2.

Required: Per metric ton of concentrates:

1. The cubic meters of air used in roasting, allowing 200 per cent excess over theoretical
2. The percentage composition of the roasted ore
3. The kilograms of lead produced
4. The kilograms of each flux required.
5. The kilograms of slag made.

327. A roasted lead ore is composed of 25 per cent PbO, 18 PbS, 22 Fe_2O_3, 2 Cu_2S, 29 SiO_2, 4 CaO. It is smelted in a blast furnace with enough $CaCO_3$ to make a slag of 18 per cent CaO. The coke used amounts to 15 per cent of the ore; it contains 89 per cent C, 11 per cent SiO_2.

Of the lead on the charge, 5 per cent is lost in the flue dust and fume, and 8 per cent enters the matte. One-half of the copper is found in the matte and one-half in the lead bullion. 10 per cent of the sulphur on the charge goes into the gases.

Required: Per 1,000 parts of ore:

1. The weight of lead bullion produced.
2. The weight of the matte.
3. The weight of $CaCO_3$ to be added.

328. A lead blast furnace produces per day 160 short tons of lead, which may be taken as 100 per cent Pb, and 28 tons of matte, which carries 9 per cent lead and 24 per cent copper. The slag carries 11 per cent CaO and the gases contain 22 per cent CO and 10 per cent CO_2. Assume that no lead or copper enters the slag and gases.

The charge consists of:

Roasted ore, per cent	Pyrite cinder, per cent	Limestone, per cent
PbO 47	Fe_2O_3 86	$CaCO_3$ 100
PbS 23	Cu_2S 6	
SiO_2 30	SiO_2 8	

The coke is 90 per cent C and 10 per cent SiO_2, and the amount used is 18 per cent of the roasted ore.

Required: 1. The weight of ore and of cinder smelted per day, in tons.

2. The percentage composition of the slag.

3. The volume of the gases per day, in cubic feet.

329. A lead blast furnace smelts the following charge:

Roasted ore (1,000 kg.), per cent	Pyrite cinder (600 kg.), per cent	Coke (180 kg.), per cent	Flux (220 kg.), per cent
PbO 31	Fe_2O_3 88	C 89	$CaCO_3$ 100
PbS 19	Cu_2S 5	SiO_2 11	
SiO_2 40	SiO_2 7		
FeO 10			

All the Cu, all the S, and 2 per cent of the Pb enter the matte. Assume no Pb in slag or gases. The metal is 100 per cent Pb. The gases contain 1 part CO_2 to 1 part CO by volume.

Required: 1. A charge balance of the furnace.

2. The proximate composition of the matte and of the slag.

3. The volume of blast used.

330. A lead ore contains 82 per cent PbS, 15 SiO_2, 3 Al_2O_3. As fluxes for smelting it, there are used limestone containing 45 per cent CaO, 2 SiO_2, 8 MgO, 1 Al_2O_3, 44 CO_2 and iron ore carrying 90 per cent Fe_2O_3, 3 SiO_2, 2 Al_2O_3, 5 MnO_2.

It is desired to have the slag contain silica, lime, and iron in the ratio

$$SiO_2 : \Sigma CaO : \Sigma FeO = 35:27:38,$$

MgO being summated with CaO and MnO with FeO.

Required: 1. The weights of lead ore, limestone, and iron ore to be used in a 2,000-lb. charge.

2. The percentage composition of the slag, including all its constituents separately.

3. The fluxing power of 100 parts of limestone in terms of available ΣCaO and of 100 parts of iron ore in terms of available ΣFeO.

331. Lead sinter is smelted in a blast furnace with a ratio of burden to coke of 10 to 1. The constituents of the burden and their analyses are as follows:

Sinter: PbO, 26.2 per cent; PbS, 15.0; FeO, 8.9; CaO, 15.6; SiO_2, 34 3.

Pyrite cinder: Fe_2O_3, 88 per cent; Cu_2S, 5; SiO_2, 7.

Limestone: CaO, 49 per cent; MgO, 5; Al_2O_3, 1; SiO_2, 3; CO_2, 42.

The coke is 87 per cent C, 11 SiO_2, 2 Al_2O_3.

Assume that all the sulphur and all the copper enter the matte. The matte will contain 5 per cent PbS. It is desired to have the slag ratio $\Sigma CaO : FeO : \Sigma SiO_2 = 20:40:30$. Summate MgO with CaO and Al_2O_3 with SiO_2 in the slag.

Required: Per 1,000 parts of sinter:

1. The weights of each of the three constituents of the burden to be taken to yield the desired slag.

2. The lead fall and the matte fall.

3. The percentage composition of the matte and of the slag.

332. A sintered lead ore is smelted in a blast furnace, with limestone and pyrite cinder as fluxes, and using 118 kg. of coke per 1,000 kg. of burden.

COMPOSITION OF MATERIALS

Roasted ore, per cent		Limestone, per cent		Pyrite cinder, per cent		Coke, per cent	
PbS	14.9	$CaCO_3$	88.0	FeS	8.5	C	84.8
$PbSO_4$	5.6	$MgCO_3$	4.4	Fe_2O_3	62.7	H	0.6
Pb_2SiO_4	27.5	Fe_2SiO_4	0.9	SiO_2	14.9	H_2O	6.3
PbO	3.9	SiO_2	4.2	Al_2O_3	5.9	SiO_2	8.3
ZnS	8.1	Al_2O_3	2.5	CaO	6.0		
Fe_2SiO_4	33.6			H_2O	2.0		
CaO	3.2						
MgO	1.9						
Al_2O_3	0.3						
Cu_2S	1.0						

Assume that the metal produced is 100 per cent Pb. Of the Pb on the charge, however, 1 per cent will be slagged (as PbO), and 4 per cent will enter the matte (as PbS). The matte will also contain all the S, all the Cu (as Cu_2S), one-third of the ZnS, iron as FeS, and an equal amount of additional iron evenly divided between Fe and Fe_3O_4.

The remainder of the zinc is slagged as ZnO. The slag ratio desired is SiO_2: CaO:FeO = 35:20:45 The blast is 5 cu. m. per kilogram of coke. Neglect fume and flue dust.

Required: 1. The weights of ore, limestone, and cinder to be used in each 1,000 kg of burden to produce the desired slag ratio

2. A complete charge balance of the furnace.

3. The percentage composition of the matte, slag, and gases

333. A blast furnace at Herculaneum, Mo., operated by the St. Joseph Lead Company, smelted a charge carrying per day 155 tons of sintered ore, 13 tons of limestone, 53 tons of pyrite cinder, 8 tons of refinery skimmings, and 28 tons of coke. These materials analyzed approximately as shown in the table below

	Sinter, per cent	Skimmings, per cent	Limestone, per cent	Cinder, per cent	Coke, per cent
PbS	18				
$PbSO_4$	6				
Pb		25			
PbO	28	75			
Cu_2S	1			2	
Fe_2O_3	19			90	
SiO_2	22		5	8	10
CaO	6				
$CaCO_3$			95		
C					90

Assume that all the sulphur goes into the matte.

In addition to the constituents tabulated, the sinter contains 80 oz of silver per ton. Assume that all the silver goes into the lead bullion.

Assume that two-thirds of the copper enters the matte and one-third enters the lead bullion.

The slag contains 10 parts FeO to 7 parts SiO_2. Neglect any lead in the slag and gases. The gases carry 1.5 parts CO to 1 part CO_2.

Required: 1. A complete charge balance of the furnace.

2. The percentage composition of each of the products.

3. The percentage of the carbon of the coke that is burned at the tuyères, assuming 90 per cent of it to go to CO and 10 per cent to CO_2.

334. In the lead blast furnace of the preceding problem, the temperature of the lead flowing from the furnace is 600°C.; of the matte, 1200°; of the slag, 1200°; and of the gases issuing from the top, 300°.

The heat content of the matte at 1000° is 200 Cal per kilogram; specific heat of liquid matte, 0.15. The heat content of the slag at 1150° is 290 Cal. per kilogram; specific heat of liquid slag, 0.26. The heat of formation of the slag is 160 Cal per kilogram of SiO_2.

Neglect heat in the entering charge and blast.

Required: A heat balance of the blast furnace.

335. A lead blast furnace smelts 100 short tons of burden per day, the burden containing 14 per cent Pb and 26 oz. of Ag per ton. The coke used weighs 10 per cent of the burden and contains 90 per cent carbon. Carbonates in the burden contain carbon amounting to 1.5 per cent of the burden. The gases coming from the top of the furnace analyze 17 per cent CO and 16 per cent CO_2. Assume that all the carbon burned at the tuyères goes to CO.

Maximum temperature in the smelting zone, 1300°C. Temperature of gases at top of furnace, 450°C. Back pressure in the furnace at the tuyères, 25 mm.

Assume that the gases in the smelting zone become one-tenth saturated with lead and silver vapor, and that their vapor pressures are not affected by any solution of silver in lead.

Required: 1. The weight of lead and silver escaping from the furnace as vapor, per day.

2. The percentage of the total lead and silver charged which is vaporized in the smelting zone.

3. At what temperature of issuing gases would all the lead and silver charged be lost as vapor?

336. Lead concentrates have the following analysis:

	Per Cent
Pb	72
Fe	5
S	14
SiO_2	3
CaO	3.3

All the Pb is present as PbS, the Fe as FeS, and the CaO as $CaCO_3$

It is desired to treat this ore by the roast-reaction method. The reactions during the roasting stage are (in addition to decomposition of the $CaCO_3$):

$$2PbS + 3O_2 = 2PbO + 2SO_2.$$

$$PbS + 2O_2 = PbSO_4.$$

$$4FeS + 7O_2 = 2Fe_2O_3 + 4SO_2.$$

At the end of this stage all the FeS has been oxidized, but only part of the PbS. The PbS that has been oxidized has been divided between the two equations above in such proportion that three times as much PbO has been formed as $PbSO_4$.

During the reaction stage the reactions are as follows:

$$PbS + 2PbO = 3Pb + SO_2.$$
$$PbS + PbSO_4 = 2Pb + 2SO_2.$$

It is aimed to continue the reaction (assume that it is so continued) until all the lead in the concentrates has been reduced to Pb, leaving no PbS, PbO, or $PbSO_4$.

Required. 1. The proximate analysis of the concentrates

2. The weight of the ore at the end of the roasting stage, and its proximate analysis, per 1,000 of original concentrates.

3. The percentage of the original sulphur that is eliminated as SO_2 during the roasting stage, and the percentage of the original PbS that remains unchanged at the end of the roasting stage.

337. At the works of the St. Louis Smelting & Refining Company, Collinsville, Ill., galena concentrates are smelted in Newnam ore hearths. The lead is reduced by the roast-reaction method:

$$PbS + 2PbO = 3Pb + SO_2$$
$$PbS + PbSO_4 = 2Pb + 2SO_2$$

The concentrates contain Pb, 72 per cent, $CaCO_3$, 6; SiO_2, 3, S, 14; Fe(as FeS), 5 They are mixed with 3.6 per cent of their weight of coke (90 per cent C and 10 per cent SiO_2). From a charge of 6,000 kg. of concentrates there are produced pig lead (100 per cent Pb) containing 67 per cent of the lead charged, slag that contains by analysis 10 per cent $PbSO_4$, 6 PbS, 25 PbO, 8.5 Pb; fume carrying 56 per cent $PbSO_4$, 2 PbS, 42 PbO; and flue dust containing 6 per cent of the lead charged and carrying 20 per cent $PbSO_4$, 58 PbS, 2 PbO

Assume the balance of the flue dust consists of CaO, SiO_2, and FeS in the same proportions as are present in the concentrates.

2½ times as much PbO as $PbSO_4$ is used in the reactions given.

Required. 1. The weight of each of the four products

2. The percentage of the total Pb charged which exists finally as PbS, as Pb, as $PbSO_4$, and as PbO, regardless of the product in which contained

3. Assuming that Pb once reduced is not reoxidized, what percentage of the total PbS charged enters into each of the reactions given?

4. What percentage of the PbO and of the $PbSO_4$ formed is used up in the reactions?

338. A Parkes desilverizing kettle receives a charge of 60 short tons of softened lead bullion, carrying 260 oz. of silver per ton. The first zinc crust is formed by adding unsaturated zinc crust remaining from treatment of a previous charge. This unsaturated crust carries 40 oz. of silver per ton and 70 per cent Pb, the balance being zinc. According to an empirical rule in the plant for bullion of this grade there is used for the first zincing enough of this crust to give 1 lb. of zinc for every 10.3 oz. of silver in the kettle after the crust is added

The lead takes up in solution, 0.52 per cent of its weight of zinc; the rest of the zinc forms the compound Ag_2Zn_3, which is removed in a crust containing 70 per cent Pb.

Pure zinc is now added in an amount sufficient to remove all the remaining silver in a crust of the same composition as the unsaturated crust first added.

The desilverized lead is pumped to a dezincing furnace, where its zinc content is oxidized and removed as ZnO mixed with 10 parts of litharge (PbO) to 1 part of ZnO.

Required: 1. The weight of unsaturated crust to be first added

2. The weight of saturated crust removed, and its silver assay, in ounces per ton.

3. The amount of zinc to be added for the second zincing, and the weight of the resulting crust.

4. The weight of pure lead finally obtained, and the percentage yield on the lead charged.

339. At the Selby Lead Works, San Francisco, Calif., a Parkes desilverizing kettle received a charge of 50 short tons of softened lead bullion carrying 160 oz. of silver per ton. The first (or saturated) zinc crust averaged 11 per cent Ag, 65 Pb, 24 Zn. This was formed by adding unsaturated crust from a previous run, without additional zinc. After its removal, enough pure zinc was added to remove all the remaining silver in an unsaturated crust of the same composition as that first added. In order that the unsaturated crusts might not accumulate, it was aimed to make the amount produced on each run equal to that required for the first zincing of the next run. The unsaturated crust contained 25 oz. of silver per ton and 70 per cent Pb, the balance being zinc. All lead takes up in solution zinc amounting to 0 6 per cent of its weight, the balance of the zinc added going into the crusts.

The desilverized lead was pumped to a dezincing furnace, where its zinc content was removed by oxidation, forming a mixture of 10 per cent ZnO and 90 per cent PbO.

The saturated crust was charged to a Faber-du-Faur retort furnace, where the zinc was distilled out, 8 per cent of it being lost by oxidation to ZnO and the remainder being recovered for use again.

The retort bullion went to cupellation furnaces, which yield fine silver The litharge from these furnaces averaged 125 oz. of silver per ton.

Required· 1 The weight of each crust, in pounds.

2. The weight of pure lead obtained for the market, and the percentage yield on the lead charged in the softened bullion

3. The weight of zinc lost on each run, and the percentage loss of the total zinc used in the two zincings.

4. The silver assay of the retort bullion, in ounces per ton.

5. The weight of fine silver obtained, and the percentage yield on that charged in the softened bullion, assuming that the market lead carries 0.2 oz of silver per ton.

340. A desilverizing kettle used in the Parkes process receives 120 metric tons of softened lead bullion, carrying 4,600 g. of silver per ton. There is added to the kettle 20 tons of unsaturated crust carrying 900 g. of silver per ton and 70 per cent lead (assume balance zinc), together with 190 kg. of pure zinc. The saturated crust then removed carries 30 per cent zinc, while the lead remaining in the kettle carries 360 g of silver per ton and 0.60 per cent zinc. Enough pure zinc is then added to remove all the remaining silver in an unsaturated crust of the same composition as that first added.

The desilverized lead is pumped to a dezincing furnace and treated for 8 hr. at a temperature of 650°C. Part of the zinc is volatilized as metallic Zn, and part is oxidized to ZnO and is raked off mixed with 10 times its weight of litharge (PbO). The furnace uses 1,800 kg. of coal per charge, the coal being 80 per cent C, 5 H, 8 O In burning the coal, 50 per cent excess air is used. Assume that the furnace gases become on the average one-sixth saturated with zinc vapor, based on the vapor pressure of zinc as it exists alloyed with lead.

Required: 1. The weight of the first zinc crust, in kilograms.

2. The weight of zinc added for the second crust.

3. Of the zinc removed in the dezincing furnace, what proportion is volatilized and what proportion is removed with the litharge? (For calculation of the vapor pressure of zinc in the alloy, see note to Prob. 319.)

4. The weight of the litharge, including its ZnO content.

341. The first (saturated) crust of Prob. 338 is charged in a Faber-du-Faur furnace and the zinc distilled out, leaving a retort bullion still carrying 1 per cent Zn; 10 per cent of the zinc in the crust is lost by oxidation as ZnO, and the remainder is recovered for use again. The retort bullion then goes to cupels where it is converted into Doré bullion that is 990 fine in silver and 3.5 fine in gold. The litharge from the cupel carries 125 oz. of silver per ton.

Required: 1. The weight, percentage composition, and silver assay of the retort bullion.

2. The weight of zinc recovered from the retort.

3. The weight of Doré bullion from the cupels.

4. The weight of gold in the Doré bullion.

5. The percentage of the silver of the charge that is in the Doré bullion, in the second crust, and in the litharge.

342. Softened lead bullion carrying 60 oz. of silver per ton is desilverized by the Pattinson process. The charge consists of 50 tons of bullion, and the products of the first crystallization are: (1) enriched alloy carrying 100 oz. of silver per ton, (2) bullion carrying 35 oz. of silver per ton, and (3) dross carrying lead equal to 3 per cent of the charge. Assume that the dross carries no silver. The bullion left in the pot after drawing off the enriched alloy consists of crystals of pure lead mixed with alloy of the same composition as that drawn off.

Each subsequent crystallization is carried to the same point, so that the assays of the enriched alloy and the bullion remaining are changed in the same ratio as in the first crystallization, and lead equal to 3 per cent of the material is removed in a dross.

Required: 1. The tons of enriched alloy and of the bullion resulting from the first crystallization.

2. The percentage of this bullion represented by solidified crystals of pure lead and by liquid enriched alloy.

3. The number of crystallizations necessary to yield enriched alloy carrying over 400 oz. of silver per ton and market lead carrying less than 0.6 oz. of silver per ton.

4. The silver assay of the final enriched alloy and market lead.

5. The number of crystallizing pots required.

6. The tons of final enriched alloy and of market lead eventually obtained from the 50-ton charge.

7. The percentage of the silver content of the charge that is lost in the market lead.

343. The electrolytic lead plant of the American Smelting & Refining Company at Barber, N. J., consisted of 96 tanks. Each tank contained 33 anodes and 34 cathodes. The cathodes were 22 by 42 in. The multiple system was used.

The tanks were connected in series, all on one circuit of 6,000 amp. at 40 volts. Current efficiency, 90 per cent.

The starting sheets were 0.1 in. thick, and the cathodes were removed after 96 hr. deposition.

Distance from anode to cathode, 1¼ in.

Required: 1. The capacity of the plant, per 24 hr.

2. The current density at the cathode.

3. The thickness of a finished cathode.

4. The resistivity of the electrolyte, in ohms per centimeter cube, assuming one-half the voltage required being due to conduction in the electrolyte.

344. A plant is to be designed for electrolytic refining of lead, with a capacity of 50 metric tons in 24 hr. The multiple system is to be used, with one 110-volt generator. The process requires the following specifications:

Current density, 200 amp. per square meter

Current efficiency, 96 per cent.

Anodes 4 cm. thick, each to be immersed in the electrolyte to a depth of 90 cm. Width of anodes, 75 cm. Nine-tenths of the weight of an anode is immersed.

Distance from anode surface to cathode surface, 5 cm.

Resistivity of electrolyte, 5 ohms per centimeter cube.

Thickness of cathode starting sheets, 1 mm.

Allow 0.1 volt for resistance of contacts, etc., in addition to electrolyte resistance.

Allow 10 cm. space of electrolyte depth below bottom of anodes, 3 cm. at each side of width of anodes, and 5 cm. between end anodes and end of tank.

A cathode will have the same immersed area as an anode.

Required: 1. The number of tanks in operation, and the number of plates per tank, allowing one more cathode than anode plate in each tank.

2. The weight of lead under treatment in the plant, not including lead content of the electrolyte.

3. The power required to operate the tanks.

4. The rate at which the temperature of the electrolyte will rise when the plant is started, neglecting heat loss from the electrolyte and assuming the specific heat of the electrolyte to be the same as that of water.

CHAPTER XXI

TRANSFER OF HEAT

The question of heat flow, or transfer, is of the utmost importance to the metallurgist. There are two distinct sides to the question, that of heat supply or useful transfer from source of heat to a body being heated, and that of heat loss or wasteful transfer from a body or furnace to the surroundings. The same principles govern both cases. There are in addition many related problems, such as the question of rate or depth of heat penetration as in heat-treating and in heating ingots or blooms for rolling, uniformity of heating or cooling, and stresses resulting from non-uniformity as in quenching, etc. In some of these problems thermal expansion enters as well as heat transfer. The discussion in this chapter will be confined to the main question of heat transmission, a quantitative understanding of which is essential.

The transfer, or passage, of heat from one place to another may take place in three different ways—by conduction, by convection, and by radiation.

Conduction of heat is the passage of heat from one part of a continuous body to another part or between two bodies in contact. This is a flow analogous to flow of electricity and in some respects also to flow of water.

Convection is the passage of heat from a body to a fluid in contact with it. The fluid may be liquid or gas; in practice it is usually air. Contact between the fluid and the hot body is involved, and thus convection is a special case of conduction, with which it is sometimes included. The important difference is that the particles of the fluid have freedom of motion while those of the solid do not. This difference entirely changes the quantitative laws governing the transfer.

Radiation is the passage of heat through space, in the form of rays, or waves. No contact is involved. This is the manner in which heat is received by the earth from the sun and in which heat is emitted by colored flame or by an incandescent body. Radiation does not require incandescence, however; heat is radiated from any body warmer than its surroundings.

Calculation of Heat Flow by Conduction.—Flow of heat from one point to another is caused by difference of temperature between the two points, and the flow will continue until equilibrium is established in the form of equal temperatures. There may be a larger number of calories in one region than in another of equal size without causing flow of heat; it is the temperature and not the quantity of thermal energy that controls heat transfer. This fact is used as a basis of defining temperature. Temperature difference is thus analogous to difference of level or of pressure, which may cause water to flow from one point to another, and to voltage or difference of potential, which may cause flow of electric current. Analogous principles apply, and analogous formulas may be used in calculation.

Computation of the quantity of heat transfer by conduction may be simple or complicated depending on the conditions. In the case of heat flowing through a homogeneous conductor of uniform cross section, so that there is a uniform temperature gradient, and well insulated at the sides, so that the heat flows only in one direction, the equation

$$Q = \frac{t_1 - t_2}{R} \qquad (1)$$

is applicable, in which Q is the quantity of heat passing between two sections whose temperatures are t_1 and t_2 and R is the thermal resistance of the conductor. It will be seen that this equation is the thermal counterpart of Ohm's law. These conditions are often approximated in furnace walls, so that the relation is a useful one.

Application of the above formula requires determination of the value of R, which is the total resistance of the section. If the dimensions of the section are known and that property of the material composing the homogeneous conductor known as the thermal resistivity can be learned, then R is given by the relation

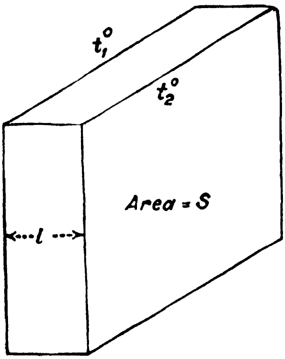

FIG. 12.

$$R = r\frac{l}{s}, \qquad (2)$$

since r, the resistivity, is the resistance of the material per unit cube and R is obviously directly proportional to l, the length of the path of flow, and inversely proportional to s, the sectional area of the path of flow. Figure 12 will clarify these relations.

In practical applications R will often be determined from relation (2), and it is therefore convenient to obtain a single equation by substituting this expression for R in Eq. (1), which gives:

$$Q = \frac{(t_1 - t_2)s}{rl}. \qquad (3)$$

In this equation, if t_1 and t_2 are expressed in degrees Centigrade and s in square centimeters and l in centimeters, then r may be in degrees per calorie per second per centimeter cube,[1] and Q will be determined in calories per second. This unit for r, however, is an awkward one and there may be used instead the "thermal ohm" per centimeter cube or per inch cube. The thermal ohm is defined as the resistance which will permit 1 watt of heat to flow when there is a temperature difference of 1°C. (1 thermal ohm = 1° per watt). With R in thermal ohms, Q is determined in watts (1 watt = 0.239 cal. per second).

The unit for s and l may be the centimeter or the inch; r must be correspondingly in thermal ohms per centimeter cube or per inch cube. The value of r per centimeter cube is 2.54 times the value per inch cube. This follows from the relation $R = r\frac{l}{s}$, in which it is seen that $\frac{l}{s}$ is not of the third degree but linear.

A purely English unit of thermal resistivity is also very commonly used. With this, r is expressed in degrees Fahrenheit per B.t.u. per square foot per inch of thickness per hour.

The value of r has been determined for many materials by various investigators. Table LI, page 423, gives some of these values. r changes with the temperature, and in the case of some materials, especially the refractories, the change is rapid. Some materials are good insulators at room temperature and fairly good conductors at yellow heat.

The units of thermal conductivity are the reciprocals of the units of resistivity:

$$k = \frac{1}{r}.$$

Thus k may be expressed in "reciprocal thermal ohms per centimeter cube," or in "calories per second per square centimeter of surface times centimeters of thickness per degree centigrade of temperature difference," or in "B.t.u. per square foot per hour per inch per degree Fahrenheit."

Practically the determination of t_1 and t_2 may offer experimental difficulties. It is not easy to measure surface temperatures. These temperatures are not the same as the temperature of the air or gases in contact with the surface and may differ widely. It is common experience that t_2, the temperature of the outside of the wall of a furnace, may be several hundred degrees above the air temperature; t_1, the temperature of the inside wall, is regularly below the temperature of the furnace chamber or the gases to which the surface is exposed.

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[1] See p. 262. An equivalent expression for the unit of thermal resistivity is "degrees per calorie per second times square centimeters of surface per centimeter of thickness."

When a furnace wall is made up of layers of different materials, so that heat escaping from the furnace must pass through each of these thicknesses, the resistances offered by the different layers are said to be in series. These resistances are additive; the total resistance of the furnace wall is the sum of the resistances of the layers. The *resistivities*, of course, must not be added, because $(r_1 + r_2)(l_1 + l_2)$ does not equal $r_1l_1 + r_2l_2$, the latter being the correct form.

When a wall is made up of different sections side by side instead of different superimposed layers, so that the escaping heat divides between the sections instead of all of it passing through all the layers, the resistances offered by the different layers are said to be in parallel. These resistances are not additive; but their reciprocals, the conductances, are. The total resistance of the wall is the reciprocal of the sum of the conductances. This principle is of importance in calculating the total resistance of the walls of a rectangular furnace.

All the heat received by a charge in a crucible or muffle must pass through the walls by conduction. A zinc retort is of regular shape with walls of uniform thickness and consequently affords a simple example. The reduction of zinc oxide within the retort absorbs heat, and the *rate* at which zinc is produced depends directly on the rate at which heat is conducted to the charge to supply the heat of the reaction. The maximum rate at which the zinc could be reduced can be calculated on the basis of certain assumptions. The actual rate will be somewhat less than this maximum, but the calculation is very useful for comparative purposes. The calculation requires the heat of the reaction *at the temperature at which it is taking place*, the temperatures of the inside and outside of the walls of the retort, the resistivity of the fire clay of which the retort is composed *at its working temperature*, and the dimensions of the retort, including the thickness of its walls.

Example 40

A zinc retort has the shape of a hollow cylinder 15 cm. in diameter and 120 cm long, inside dimensions. It is made of fire clay, with a resistivity of 80 thermal ohms at the working temperature. An average temperature of 1200°C. is maintained inside the retort, requiring a temperature of 1250° on the inside surfaces of the walls. The outside surfaces are at 1500°C.

Assume that the reduction takes place in accordance with the equation $ZnO + C = Zn + CO$.

Required: 1. The heat entering the retort through the walls, per hour, (*a*) if the walls are 4 cm. thick; (*b*) 2 cm. thick.

2. The maximum rate at which zinc could be reduced per hour, in each case.

3. The outside temperature which would be necessary to produce a maximum of 3 kg. of zinc per hour, in each case.

Solution: In calculating the area of the path of heat flow through the walls of the retort, account must be taken of the fact that heat may enter through the closed end of the retort as well as through the sides. Thus the area *s* of the cylindrical retort will be made up of the sum of the two quantities $2\pi rl$ and πr^2, where l is the length of the cylinder and r is its radius.

It must be observed also that the area s which determines the mean path of heat flow is neither the outside area nor the inside area of the retort, but a mean between them. For most purposes it will be sufficiently accurate to calculate s by using the simple *arithmetical* mean values of l and r, and this method will be shown first below. However, a consideration of the geometry involved shows that in the case of cylinders the mean area is given more precisely by the *logarithmic* mean between the inside and outside surfaces. This more precise method will also be shown below. (This question is discussed further on p. 318, where an expression based on the inside and outside diameters and the outside length of the cylinder is given.)

In case a the arithmetical mean value of r will be the mean between $\frac{15}{2}$ and $\frac{23}{2}$, or 9.5 cm., and the mean value of l will be the mean between 120 and 124, or 122 cm. Similarly, in case b, r will be 8.5 cm., and l will be 121 cm.

Then.

$$\text{Case } a\text{: } s = 2\pi \times 9.5 \times 122 + \pi \times 9.5 \times 9.5 = 7{,}560 \text{ sq. cm.}$$

$$\text{Case } b\text{: } s = 2\pi \times 8.5 \times 121 + \pi \times 8.5 \times 8.5 = 6{,}690 \text{ sq. cm.}$$

$$t_1 - t_2 = 1500^\circ - 1250^\circ = 250^\circ$$

$$\text{Case } a\text{: } Q = \frac{250 \times 7{,}560}{80 \times 4} = 5{,}900 \text{ watts} = 5{,}080 \text{ Cal. per hour.}$$

$$\text{Case } b\text{: } Q = \frac{250 \times 6{,}690}{80 \times 2} = 10{,}450 \text{ watts} = 9{,}000 \text{ Cal. per hour (1).}$$

The more precise method using the logarithmic mean area is as follows:

Case a: The inside area $s_1 = 2\pi \times 7.5 \times 120 + \pi \times 7.5 \times 7.5 = 5{,}832$ sq. cm.

The outside area $s_2 = 2\pi \times 11.5 \times 124 + \pi \times 11.5 \times 11.5 = 9{,}376$ sq. cm.

$$\text{The logarithmic mean is } \frac{s_2 - s_1}{2.3 \log \frac{s_2}{s_1}} = 7{,}473 \text{ sq. cm.}$$

$$\text{Case } b\text{: } s_2 = 2\pi \times 9.5 \times 122 + \pi \times 9.5 \times 9.5 = 7{,}566 \text{ sq. cm.}$$

$$\text{The logarithmic mean is } \frac{7{,}566 - 5{,}832}{2.3 \log 1.298} = 6{,}669 \text{ sq. cm.}$$

When these mean values are used for s, Q in case a becomes 5,840 watts, or 5,020 Cal. per hour, and Q in case b becomes 10,410 watts, or 8,960 Cal. per hour (1).

$$\begin{array}{llll} ZnO + C = & Zn + CO & & \\ 83{,}500 & -29{,}160, & & \Delta H = 54{,}340. \end{array}$$

This is the heat of the reaction at 18°C. From this there must be subtracted the heat contents of 81.4 kg. of ZnO and 12 kg. of C at 1200°; and there must be added the heat contents of 65.4 kg. of Zn and 28 kg. of CO at 1200°. The results give: 54,340 − 11,640 − 5,350 + 37,520 + 8,830 = +83,730 Cal., the heat of the reaction at 1200°

$$\text{Therefore, to reduce 1 kg. of zinc requires } \frac{83{,}730}{65.4} = 1{,}280 \text{ Cal.}$$

The maximum amount of zinc reduced is:

$$\text{Case } a\text{: } \frac{5{,}020}{1{,}280} = 3.9 \text{ kg. per hour.}$$

$$\text{Case } b\text{: } \frac{8{,}960}{1{,}280} = 7.0 \text{ kg. per hour (2).}$$

To produce 3 kg., 3 × 1,280 = 3,840 Cal. required per hour = 4,470 watts.

$$\text{Case } a\text{: } 4{,}470 = \frac{(t_1 - 1{,}250)7{,}473}{80 \times 4}. \qquad t_1 = 1442^\circ\text{C}.$$

$$\text{Case } b\text{: } 4{,}470 = \frac{(t_1 - 1{,}250)6{,}669}{80 \times 2}. \qquad t_1 = 1359^\circ\text{C. (3).}$$

Limitations and Extensions.—The limited conditions under which the method just illustrated can be applied with precision have been noted on page 314, and there has been suggested the upsetting influence of inaccuracies in data—factors that usually are experimentally difficult to allow for, with any degree of confidence. But more must be said in this connection.

The quantity $\frac{s}{l}$ in Eq. (3), page 314, may be called the "shape factor." When the conductor is not of regular shape so that either s or l varies in different parts of it, the shape factor is no longer definitely known. Furthermore, in a walled body such as a furnace, where s is divided into different parts—one part for each wall—the condition of heat flow in one direction only is no longer fulfilled. Heat then flows in different directions at the corners where the walls meet, altering the relations of s and l. If l is very small in proportion to s, as in a large reverberatory furnace, for example, the error involved is negligible. But in a furnace of relatively small chamber and thick walls, as in converters and most electric furnaces, a correction must be applied. In general, even though s and l may not be accurately known, it may be possible through some assumption to arrive at a fairly accurate value of the ratio $\frac{s}{l}$. In the case of certain regular shapes often occurring in practice, corrections for $\frac{s}{l}$ have been worked out, partly mathematically and partly experimentally, by Langmuir, Adams, and Meikle.[1] In the case of coaxial cylinders, as a zinc retort, they found that the ratio $\frac{s}{l}$ should be replaced by $\frac{2\pi c}{\ln b/a}$, where b is the outside diameter, a the inside diameter, and c the outside length of the cylinder. $\left(\text{This expression reduces to } \frac{2.73c}{\log b/a}.\right)$

In the case of concentric spheres, no modification of $\frac{s}{l}$ is required, other than the precaution of taking for s the geometric mean between the inside and outside surface areas, as determined by the square root of their product.

In the case of a rectangular prism (*i.e.*, a straight-walled chamber as exemplified in many small furnaces), the value of $\frac{s}{l}$ must be increased to allow for the heat conducted through the corners. The proper increment was found to be $1.2l + 0.54\Sigma e$, where Σe is the total length of all 12 inner edges of the furnace chamber. The shape factor thus becomes $\frac{s}{l} + 1.2l + 0.54\Sigma e$. This applies when l is not more than five times the length of any one of the inner edges, so that it is practically always applicable. In this expression, however, s is the area of the *inside* surface, not the mean area as above.

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[1] "Flow of Heat through Furnace Walls: the Shape Factor," *Trans. Am. Electrochem. Soc.*, **24**, 53 (1913).

A more general form of Eq. (3), applicable when the temperature of the material is not constant and r varies with the temperature, is:

$$Q = \frac{s}{l}\int_{t_1}^{t_2}\frac{dt}{r}.$$

General Equation of Heat Conduction.—The foregoing discussion has dealt with flow of heat in one direction or with such change in direction as could be allowed for and expressed in the terms of unidirectional flow. The most general case, however, is of heat flowing in all directions, as to or from the interior of a body. This case is encountered in practice, for example, in cooling ingots or, in the reverse direction, in heating ingots, as for rolling, pressing, or forging. In an example of this kind, it is more often the calculation of temperatures at different points of the body, rather than quantity of heat flow, that is desired.

Following is the general equation of heat conduction given by Preston[1]:

$$c\frac{dT}{dt} = \frac{l}{r}\left(\frac{d^2T}{dx^2} + \frac{d^2T}{dy^2} + \frac{d^2T}{dz^2}\right),$$

in which x, y, and z are the distances along the three axes of space, c is the heat capacity of the body per unit volume, and t is the time. Practical use of this equation to determine the temperature T at any point located by numerical values of x, y, and z, after a definite time represented by a numerical value of t, requires knowledge of other conditions, particularly those of heat flow at the surface, which will permit integration of the equation. Reference must be made to more specialized works on heat for further discussion of this subject.

Heat Loss by Convection and Radiation.—Whereas conduction deals with flow of heat *through* a body, convection and radiation have to do with transfer of heat from (or to) the *surface* of a body. In most cases loss of heat from a surface will occur by convection and radiation simultaneously, the total loss being the sum of the two parts. Investigation has shown that for heat actually at the surface, so that conduction in any part of the body itself is nil, the loss by convection is independent of the nature of the surface but does depend on the shape and position of the surface. Loss by radiation, on the other hand, is independent of the shape and position but does depend on the nature of the surface.

[1] "Theory of Heat," 3d ed., p. 643, Macmillan & Co., Ltd., London, 1919.

The temperature of the surface is, of course, a principal factor in both cases. In general the portion of the total loss due to convection is greater than that due to radiation when the temperature of the surface is relatively low, but the radiation loss increases more rapidly than convection with increase of temperature and soon becomes the major portion. At some temperature the loss is evenly divided between convection and radiation, but where this temperature lies cannot be stated definitely as conditions alter it greatly. It can be determined by calculation.

Calculation of Convection Loss.—In an early investigation[1] of convection, Dulong and Petit gave the empirical formula

$$Q_c = n(t_2 - t_1)^{1\ 233},$$

in which Q_c is the quantity of heat lost by convection per square centimeter of surface per second, t_2 is the temperature of the surface and t_1 of the surrounding air, and n is a constant depending on the shape and position of the surface. Values of n were later (1860) determined by Péclet, and the results have been widely used in calculation of convection, though indications that Péclet's values were too low have resulted in more or less arbitrarily increasing them.

More recently Langmuir[2] approached convection loss from the standpoint of its being a special case of conduction and calculable on the same principles if proper values for l, the thickness of the film of air (or other fluid) adjacent to the surface and passed through by the heat, were taken, in conjunction with its resistivity. He recognized, however, as did the early investigators, that the formula must include a constant as a shape factor.

Langmuir's formula is stated in the form

$$Q_c = S(\phi_2 - \phi_1),$$

in which ϕ_2 and ϕ_1 are values for the thermal conduction of the air (or other fluid) at the temperatures t_2 (of the surface) and t_1 (of the air) and S includes the shape factor and a quantity B equal to the thickness of the air film.

For the values of S in the case of cylinders and spheres, the reader is referred to Langmuir's article. The use of the formula in the case of plane surfaces, such as furnace walls, will be taken up here. In this case the formula is stated thus:

$$Q_c = \frac{\phi_2 - \phi_1}{B} \text{ watts per square centimeter.}$$

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[1] *Ann. chim. phys.*, **7** (1817).

[2] "Convection and Radiation of Heat," *Trans. Am. Electrochem. Soc.*, **23**, 299 (1913).

For a vertical surface, $B = 0.45$ cm.
For a horizontal surface facing up, $B = 0.41$ cm.
For a horizontal surface facing down, $B = 0.92$ cm.

These values of B were found to be nearly independent of the temperature unless the difference between t_2 and t_1 is less than 50°C. Then the value of B rises, making the calculated convection too high.

Langmuir's table[1] for the value of ϕ is given below, showing the values at different temperatures and for different gases.

TABLE V.—THERMAL CONDUCTION FACTOR (ϕ) OF GASES FOR CALCULATION OF HEAT TRANSFER BY CONVECTION
(In watts per centimeter)

T, °K.	Air	Hydrogen	Mercury vapor	Nitrogen	Carbon dioxide
0	0.0000	0.0000	.....	0.0000	0.0000
100	0.0041	0.0329	.....	0.0054	0.0036
200	0.0168	0.1294	.....	0.0188	0.0082
300	0.0387	0.278	......	0.0417	0.0207
400	0.0669	0.470	...	0.0717	0.0390
500	0.1017	0.700	0.0165	0.1081	0.0635
700	0.189	1.261	0.0356	0.1989	0.1318
900	0.297	1.961	0.0621	0.3119	0.2274
1,100	0.426	2.787	0.0941	0.4450	0.3620
1,300	0.576	3.726	0.1333	0.5980	0.5455
1,500	0.744	4.787	0.1783	0.7710	0.7325
1,700	0.931	5.945	0.228	0.9620	0.9370
1,900	1.138	7.255	0.284	1.172	1.117
2,100	1.363	8.655	0.345	1.401	1.363
2,300	1.608	10.18	0.411	1.649	1.634
2,500	1.871	11.82	0.481	1.918	1.932
2,700	......	13.56	0.556	2.202	
2,900	......	15.54	0.636	2.511	
3,100	......	17.42	0.719	2.834	
3,300	......	19.50	0.807	3.176	
3,500	....	21.79	0.898	3.540	

In the case of metallurgical furnaces, the temperature given by T in the table will usually lie between 300 and 900°K., and the gas to which the heat is passing will usually be air. In Fig. 13 there is given a plot of the value of ϕ against temperature, from the data of the first two columns of the table. An equation that gives accurately the values of ϕ for temperatures from 300 to 900°K. in air is as follows:

$$\phi_T = 0.00015\left(\frac{T}{1{,}000}\right) + 0.46775\left(\frac{T}{1{,}000}\right)^2 - 0.135\left(\frac{T}{1{,}000}\right)^3 + 0.025\left(\frac{T}{1{,}000}\right)^4.$$

---

[1] *Ibid.*

The above discussion and formulas all apply to convection under still conditions, where there is no motion of the air (or other fluid) other than that, presumably, due solely to convection currents. If the surface is in a draft of moving air, convection increases rapidly. The amount of cooling possible by blowing air on a hot surface is surprisingly large, a fact of which automotive engineers and others have taken full advantage. Langmuir found that the heat loss by convection from a vertical plane surface in moving air is approximately $\sqrt{\frac{35 + V}{35}}$ times the loss in still air, where V is the velocity of the air current in centimeters per second. It is indicated that this relation can be applied to other surfaces with fair accuracy.

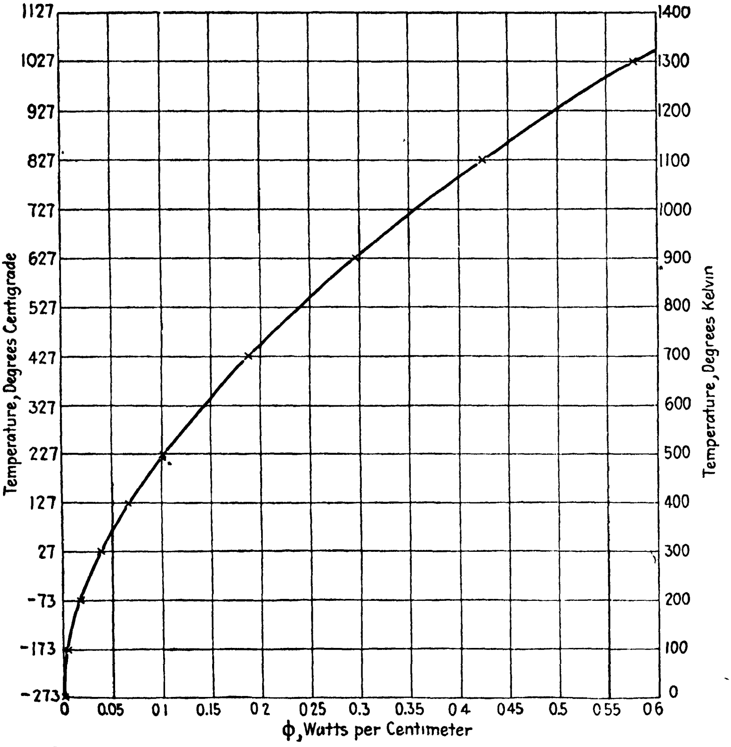

Fig. 13.—Variation of ϕ, the thermal conduction factor for heat transfer by convection in air, with temperature.

Calculation of Radiation Loss.—For calculation of quantity of heat transferred by radiation, the well-known fourth-power law, set forth by Stefan in 1879 and mathematically demonstrated by Boltzmann in 1884, has been universally adopted. The law is expressed in the formula

$$Q_R = 5.76E\left[\left(\frac{T_2}{1{,}000}\right)^4 - \left(\frac{T^1}{1{,}000}\right)^4\right] \text{ watts per square centimeter,} \quad (4)$$

in which T_2 and T_1 are the temperatures of the surface and the surroundings in degrees Kelvin and E is a fraction called the "emissivity," depending on the nature of the surface.[1]

If it is assumed that the temperature of the surface can be learned with reasonable accuracy, practical use of this formula hinges on the the proper value of E. When a body will absorb all heat radiated to it, without reflecting or rejecting any of it, it will also emit heat by radiation at a maximum rate. While this is an ideal condition probably not wholly attained in nature, it is approximated by lampblack and other closely similar surfaces that are both dull and black. Such an ideal surface is called a *black body;* its emissivity is 1. If a surface is either light in color or polished, its reflecting power rises and its emissivity becomes lower; its emissivity is expressed as a fraction of that of the ideal black body. Values of E have been experimentally determined for many kinds of surfaces; some of them are given in Table LII, page 424.

E may be determined with a radiation pyrometer, if the *true* temperature of the surface is known. Let T_A be the true temperature and T_P be the temperature indicated by the pyrometer. Then:

$$E = \frac{\text{actual radiation}}{\text{radiation if surface were a black body}} = \frac{T_P{}^4 - T_1{}^4}{T_A{}^4 - T_1{}^4}.$$

T_P is sometimes called the "black-body temperature," distinguishing it from the true temperature of a surface. It is related to the true temperature as follows:

$$T_P = \sqrt[4]{ET_A{}^4 + (1 - E)T_1{}^4}.$$

E is not entirely independent of temperature but does not vary in any regular manner, and in most cases the variation is not seriously large if the temperature difference is not too great. Values are given at different temperatures in Table LII. Some of the differences noted may be due to temperature, and some to differences in the surfaces used

Any body wholly enclosed, as in a furnace, acts like a black body when its temperature is constant, as it is then emitting all the hea received by radiation.[2]

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[1] The constant 5.76, commonly denoted by σ, was formerly given the value 5.9 Later determinations have all been lower. Landolt and Bornstein ("Erganzungs band," W. A. Roth and K. Scheel, Julius Springer, Berlin, 1927) give 5.76 as the mos probable value, being the mean of four recent determinations ranging from 5.73 t 5.80.

[2] For discussion and proof, see Preston, *op. cit.*, p. 554.

Heat Loss and Surface Temperature in a Furnace.—The heat lost from a furnace through its walls must first pass by conduction through the walls to the outer surface and then must be dissipated to the surroundings by convection and radiation. If Q_K is the heat conducted through the walls:

$$Q_K = Q_C + Q_R. \tag{5}$$

If any two of these quantities are found, the third is thereby determined. This method may sometimes be used to obtain information about emissivity, resistivity, or other factors involved. However, it is important to note that the temperature of the outside surface is a necessary datum for calculation of each of the three quantities above—except that, as shown below, Q_K may sometimes be determined in a wholly different manner. The outside-surface temperature is the *lower* temperature in the discussion of conduction, and it is the *higher* temperature in the discussion of convection and radiation. Obviously a higher surface temperature lowers Q_K but increases Q_C and Q_R. Therefore, there can be only one value of the surface temperature which will satisfy the relation of Eq. (5) above. When steady conditions of heat flow and dissipation have been established, the surface temperature is fixed, and it is a function of the heat being lost, Q_K. This indicates the possibility of simultaneous determination of the surface temperature and Q_K when both are unknown. The data available, however, must include all the other factors necessary for calculation of conduction, convection, and radiation. These are: for conduction, the thickness, area, and resistivity of the furnace walls, and the inside wall temperature; for convection, the area only (assuming still air outside at about 20°C.); for radiation, the area and the emissivity of the surface.

If it is known that a furnace must be operated at a certain temperature inside, say 1200°C., and if the dimensions of its walls and the material of which they are composed, also the emissivity of the outside surface, are known, then the loss of heat by conduction and the temperature of the outside surface can be calculated. An example illustrating this calculation will be given below.

In the case of an electric-resistance furnace, the heat lost through the walls, Q_K, is approximately the power required to operate the furnace at its working temperature, apart from any heat requirements of the charge. If the temperature of the furnace is remaining approximately constant and no action absorbing or generating heat is taking place in the charge, then the power input is being just balanced by the heat losses. In many furnaces the heat losses would be largely accounted for by conduction through the walls. In arc furnaces allowance would have to be made for heat lost through the electrodes and perhaps also in escaping gases. In special cases, therefore, the power input can be used to determine the heat conducted through the walls without knowledge of dimensions or resistivity.

Example 41

At the operating temperature of a furnace the inside surface of the walls is at 1200°C. The furnace is rectangular, its chamber measuring 40 by 50 by 120 cm. Each wall is 10 cm. thick and is made of refractory having a resistivity of 160 thermal ohms per centimeter cube at its average working temperature.

The outside of the furnace is covered with thin sheet iron, partly rusted, having an emissivity of 0.70. Assume the temperature of the surrounding air to be 27°C

Required: The total heat loss by conduction through the walls (neglecting any difference due to the door), and the temperature of the outside surface of the furnace.

Solution:

$$Q_K = \frac{(t_1 - t_2)s}{rl} = \frac{(1{,}200 - t_2)s}{160l}. \qquad (1)$$

In this formula use for $\frac{s}{l}$ the shape factor given on page 319, *viz.*, $\frac{s}{l} + 1.2l + 0.54\Sigma e$.

s is found from the dimensions given to be 25,600 sq. cm., and Σe is 840 cm. Equation (1) then becomes:

$$Q_K = 18.9(1{,}200 - t_2) \qquad (2)$$

$$Q_C = \frac{\phi_2 - \phi_1}{B}. \qquad (3)$$

$$\begin{aligned} Q_R &= 5.76E\left[\left(\frac{T_2}{1{,}000}\right)^4 - \left(\frac{T_1}{1{,}000}\right)^4\right] \\ &= 4.03\left[\left(\frac{T_2}{1{,}000}\right)^4 - 0.3^4\right] \\ &= 4.03\left(\frac{T_2}{1{,}000}\right)^4 - 0.0335. \end{aligned} \qquad (4)$$

Algebraically the solution of the problem now would consist of setting Eq (2) equal to the sum of Eqs. (3) and (4) and solving for the unknown $T_2 (= t_2 + 273)$ But this procedure would require the expression of Eq. (3) in different terms. It will be much more convenient to make a graphical solution of the equations. We shall plot a curve giving the values of Q_K for different values of T_2 in Eq (2). We shall plot another curve giving the values of $(Q_C + Q_R)$ for different values of T_2. Since there is but one value of T_2 satisfying both these relations, the two curves must intersect; the locus of their point of intersection gives the solution for both T_2 and Q_K.

From Eq. (2):

When T_2 = 300°K. = 27°C. Q_K = 22,200 watts.
When T_2 = 400°K. = 127°C., Q_K = 20,300 watts.
When T_2 = 500°K. = 227°C., Q_K = 18,400 watts.
When T_2 = 600°K. = 327°C., Q_K = 16,500 watts.

These values are plotted in Fig. 14.

From Eq. (4):

When T_2 = 300°K., Q_R = 0.
When T_2 = 400°K., Q_R = 0.0703 watt per square centimeter = 3,150 watts total.
When T_2 = 500°K., Q_R = 0.2190 watt per square centimeter = 9,810 watts total.

When $T_2 = 600°K.$, $Q_R = 0.522$ watt per square centimeter = 23,400 watts total

In Eq. (3):

For Q_C, refer to Table V, page 321, for the values of ϕ_2 and ϕ_1. The values of B for the different walls are those shown on page 321.

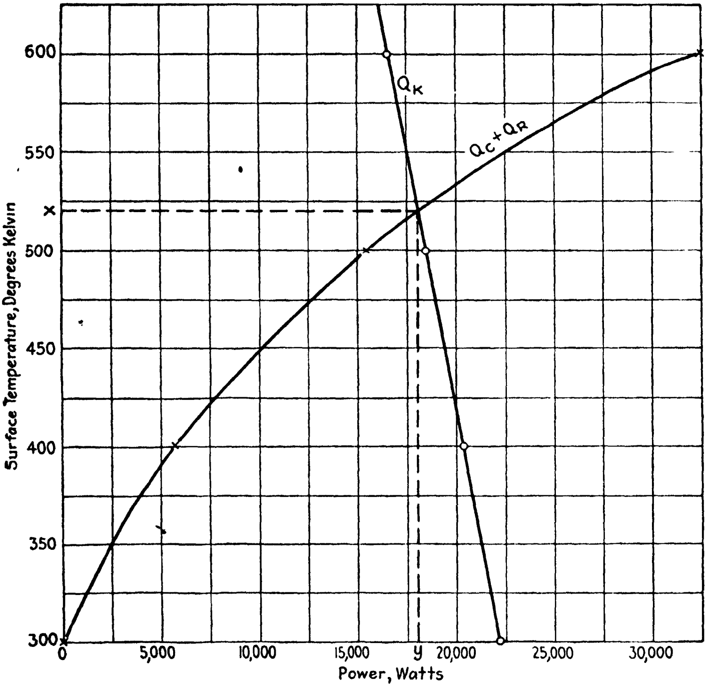

FIG. 14.—Determination of power requirement and outside surface temperature (Example 41).

At 27°C. (= 300°K.): $\phi_1 = 0.0387$.

At 300°K.: $\phi_2 = 0.0387$. $Q_C = \frac{\phi_2 - \phi_1}{B} = 0$.

At 400°K.: $\phi_2 = 0.0669$. $Q_C = \frac{0.0282}{B}$ watt per square centimeter

$$\text{Total } Q_C = \frac{0.0282}{0.45} \times 25{,}200 + \frac{0.0282}{0.41} \times 9{,}800 + \frac{0.0282}{0.92} \times 9{,}800 = 2{,}550 \text{ watts.}$$

Similarly:

At 500°K.: Q_C = 5,700 watts.
At 600°K.: Q_C = 8,990 watts.

Adding the above values:

For 300°K.: $Q_C + Q_R = 0$
For 400°K.: $Q_C + Q_R$ = 5,700 watts.
For 500°K.: $Q_C + Q_R$ = 15,500 watts.
For 600°K.: $Q_C + Q_R$ = 32,400 watts.

These values are also plotted in Fig. 14, where it is seen that their curve intersects that of Q_K at the point given by:

$$W_K = 18{,}000 \text{ watts.}$$
$$T_2 = 520^\circ\text{K.} = 247^\circ\text{C.}$$

Accordingly, the heat conduction through the furnace walls is 18,000 watts (= 4,300 cal. per second), and the temperature of the outside surface of the walls is 247°C.

Calculation of the Size of Electrical Conductors and Resistors.—For the installation of conductors to carry heavy currents, such as power-transmission lines or the bus bars in electrometallurgical plants, it is necessary to determine the proper cross-sectional area for the conductor. Using too large a conductor involves a waste of valuable metal manifested in excessive plant-investment cost; in some cases it may result in other bad features such as increase of wind resistance and ice accumulation and the necessity of stronger supports. On the other hand, too small a section results in excessive power loss (I^2R) in the conductor and may cause the conductor to become too hot.

Kelvin's law constitutes a first approach to this problem. It states that "the most economical size of conductor is that for which the annual investment charges are equal to the cost of energy lost in the conductor per year." Since the law considers only the interest charges and the I^2R loss, ignoring other important factors, it is not regarded as a satisfactory basis for design. Its use is often desirable, however, in arriving at a preliminary result, which may then be modified by other considerations as necessary.

A mathematically equivalent statement of Kelvin's law would be that the most economical size of conductor is that for which the sum of the annual investment charges plus the cost of energy lost is a minimum. In the problems below either form of the statement may be applied; if the latter form is used, the problem becomes one in maxima and minima, in the solution of which an equation will be established in which the first derivative is set equal to zero.

Further light may be thrown on the problem of the proper size of conductor by calculating the temperature rise in the conductor resulting from the I^2R loss. While Kelvin's law itself does not deal with heat transfer, the calculation of temperature rise, which sometimes forms a useful adjunct to the law, makes it desirable to include the problem in this chapter. The *rate* of temperature rise is obtained by dividing the I^2R loss by the heat capacity of the conductor. The final temperature reached by the conductor may be calculated by equating the I^2R loss to the heat dissipated from the surface of the conductor by radiation and convection. The temperature of the conductor will continue to rise until its surface temperature is just sufficient to disperse all the heat being generated in it. Solution of the resulting equation accordingly determines the temperature reached, Calculation of the size of resistor (heating element) needed for an electric-resistance furnace is based on the same principles. In this case the resistor must be small enough to generate the required quantity of heat (I^2R) at a given current and to reach the temperature needed for the furnace; but it must be large enough so that its temperature will not rise too rapidly or too far under the existing conditions of heat transfer from the resistor to the furnace charge and to the surroundings.

Problems

345. A charge of zinc ore in a retort requires 20,000 kg.-Cal. for heating up to the operating temperature and absorbs 33,000 kg.-Cal. in reduction to zinc vapor. The time required is 13 hr. for the reduction period. During this period the average temperature inside the retort is 1200°C. and outside the retort 1300°C.

The retorts have a logarithmic mean periphery of 72 cm. and are 150 cm. long. The walls are 3 cm. thick. Neglect the ends.

Required: 1. The resistivity of the retort material in degrees per gram-calorie per second times square centimeters per centimeter of thickness, and in thermal ohms per centimeter cube.

2. The time required for heating up to the operating temperature of 1200°, assuming the average temperature during the heating period to be 50 per cent above the arithmetic mean (starting at 0°) during the heating period inside the retort and to remain constant at 1300° outside.

346. A zinc retort is 5 ft. long, with walls 1.5 in. thick, and 2.6 ft in mean active periphery. The charge contains 75 lb. of zinc and requires 45,000 Cal. for its treatment. The average difference in temperature between the inside and outside of the retort is 100°C. The average thermal resistivity of the retort material is 35 thermal ohms per inch cube.

Required: The number of hours required for the treatment of the charge.

347. A zinc retort has walls 1.1 in. thick. The resistivity of the retort material is 0.10°F. per B.t.u. per square foot per inch thickness per hour The heat required by the charge during active reduction is 82,000 lb.-cal per 65 lb. of zinc produced. The mean conducting surface area of the retort is 10 sq. ft. Zinc is produced in full operation at the rate of 5.5 lb. per hour.

Required: The difference in temperature between the inside and outside surfaces of the retort.

348. A zinc-reduction works has retorts that are cylindrical with circular cross sections, 25 cm. inside diameter and 32 cm. outside diameter, 140 cm. long. They are made of fire clay with a thermal resistivity at the working temperature of 95 thermal ohms. The outside surfaces of the retorts are at a temperature of 1410°C., while the temperature at which the zinc vapor comes off the charge is 1300°C.

The reduction equation is:

$$\mathrm{ZnO} + \mathrm{C} = \mathrm{Zn} + \mathrm{CO}; \qquad \Delta H_{1800} = 81{,}600 \text{ Cal}$$

The condensers have the shape of truncated cones 50 cm. in length, 35 cm. inside diameter at one end and 9 cm. inside diameter at the other end, and have walls 2.5 cm. thick. Their resistivity is 150 thermal ohms.

Required: 1. The maximum rate at which heat can pass through the walls of a retort, per hour.

2. The maximum rate at which zinc can be produced in one retort, per hour.

3. If the CO leaves the condenser at 300°C. and the average inside temperature of the condenser is 650°C., what must be its average outside temperature to disperse the heat left in it by the zinc and CO when the retort is working at its maximum zinc output, assuming the gases entering the condenser to be at 1100°?

349. An all-metal thermos bottle of 1 qt. (57.75 cu. in.) capacity consists of a cylinder 2.5 in. in diameter, with thin metal walls, surrounded by a vacuum ¼ in. in thickness. Neglect the neck of the bottle and assume conduction through the top the same as through the bottom. Assume that the mean diameter for calculation of conducting area is at the center of the vacuum chamber. Resistance of metal parts negligible. Temperature of outside air, 60°F.

Required: 1. When the bottle is filled with water at 32°F., how long will it take for the water to reach 50°F.?

2. When the bottle is filled with water at 180°F., how long will it take for the water to reach 70°F.?

3. The same as requirement 2, but with insulation of powdered magnesia instead of a vacuum.

Resistivity of vacuum = 6,700 thermal ohms per inch cube. Resistivity of powdered magnesia = 520 thermal ohms per inch cube.

350. 1. A flow of slag gives with the radiation pyrometer a black-body temperature of 1100°C. If its emissivity is 0.65, what is its actual temperature?

2. A piece of oxidized sheet iron, at an actual temperature of 900°C., gives a black-body temperature of 850°. What is the emissivity at 900°?

351. Zinc concentrates (assume pure ZnS) are roasted without fuel at a temperature of 850°C.; the roasting action begins at 550°C. The ore pieces are of such size as to average 0.8 sq. cm. free radiating surface and become coated with ZnO as soon as roasting begins, the oxidation proceeding toward the center. 100 per cent excess air is used.

Assume that the temperature of the air used for the oxidation and of the surroundings is 100°C. and that each piece is free to radiate heat. Heat is lost from the ore by radiation and as sensible heat in the gases formed by the roasting. Allow also for the heat absorbed by the ZnO.

Emissivity of ZnO = 0.50.

Required: 1. The grams of ZnS which must be roasted per minute in each piece to maintain the temperature of 850°C.

2. The amount which must be roasted to maintain a temperature of at least 550°C.

3. Roasting 0.5 g. per minute per piece, what temperature would result?

352. A polished nickel sphere 6 in. in diameter is to be heated to 1000°C. Its temperature when placed in the furnace is 50°C. The atmosphere and walls of the furnace are at 1300°C. and may be assumed constant. The ball is suspended by a thin wire so that it receives heat only by radiation and convection.

For spheres:

$$W_c = S(\phi_1 - \phi_2) \text{ watts,}$$

where $S = \frac{\pi d^2}{0.45}$.

Required: 1. The calories received by the sphere, per second, just after heating begins.

2. The same just before heating ends.

3. The approximate time required to reach 1000°C., based on the assumption that the average rate at which the sphere receives heat is the arithmetic mean between the results of requirements 1 and 2.

353. An electric muffle furnace has an inside opening 5 by 8 by 20 in. The insulating walls, 5 in. thick, have a thermal conductivity of 2.4 B.t.u. per square foot per hour per inch thickness per degree Fahrenheit.

Temperature of inside of furnace = 2060°F.
Temperature of outside of furnace = 260
Temperature of air = 80

Required: 1. The amount of electrical energy required to operate the furnace.

2. The amount lost at the surface of the furnace by convection and by radiation.

3. What will be the emissivity of the surface of the furnace?

4. If the surface is changed to polished nickel, with $E = 0.05$, what will be the power used and the temperature of the outside of the furnace?

354. An electric furnace for melting brass is circular with flat top and bottom, 2 m. in diameter by 2 m. high. It hangs on trunnions (neglect conduction through trunnions). Floor and surroundings assumed at 27°C.

The surface is black iron, painted glossy black, with emissivity of 0.75. When the paint wears off, the emissivity of the rusty iron surface is 0.85. When it is painted with aluminum paint, the emissivity is 0.45. Power on furnace, 50 kw. Assume outside temperature of shell uniform all over, at 150°C.

Required: 1. The convection losses from the outside surface in calories per second and in kilowatts.

2. For each kind of surface, the radiation losses in calories per second and in kilowatts.

3. Tabulate these, with the total losses in calories per second and in kilowatts.

4. The net melting efficiency.

5. How much could the power on the furnace be reduced when the furnace is painted with aluminum paint if the melting efficiency is not increased above the value for a rusty iron surface, the surface temperature remaining at 150°C.?

355. A roasting furnace of the Wedge type roasts 40 tons of concentrates in 24 hr. It consists of a cylindrical shaft 22 ft. in diameter and 24 ft. in height, outside dimensions, supported on steel columns. The walls are of firebrick, 8 in. thick, covered with ½-in. steel plate. Assume all heat conducted through the walls is dissipated by radiation and convection, this heat amounting to 290,000 Cal. per ton of concentrates roasted.

Resistivity of firebrick, 90 thermal ohms per centimeter cube. Resistance of steel plate negligible. Emissivity of outside steel surface, 0.80. Temperature of surroundings, 27°C.

Required: 1. The difference in temperature between the inside and outside of the furnace walls.

2. The actual temperature of the inside and outside of the furnace walls.

356. An electric brass-melting furnace is to be spherical, with the roof lined with 9 in. of Sil-O-Cel and 4 in. of firebrick and the hearth with 9 in. of Sil-O-Cel and 8 in. of firebrick. The furnace is filled with molten brass just to the top of the 8-in. layer of firebrick.

Working temperature inside, 1250°. Heat to melt cold brass, 135 Cal. per kilogram. Specific gravity of melted brass, 8.0.

Outside diameter, 6 ft. The shell is of wrought iron, ½ in. thick. Outside temperature, 27°. (The resistance of the wrought-iron shell is negligible.)

Required: 1. The pounds of molten brass contained in the furnace.

2. The theoretical power required to melt this quantity in 4 hr.

3. The power loss from the furnace.

357. A copper bus bar is required to carry 7,000 amp. and will be used at an average temperature of 30°C. Bus-bar copper costs 20 cts. per pound, and power costs 7.5 mills per kilowatt-hour. Interest rate, 5 per cent.

The standard electrical resistivity of copper is 0.000001724 ohm per centimeter cube (1 cm. long by 1 sq. cm. area) at 20°C. The temperature coefficient of resistance is 0.00393 per degree centigrade at 20°C.

Required: 1. The area of cross section (in square inches) of the most economical size of bar, according to Kelvin's law.

2. The value of the power loss per year, per 1,000 ft. of bus bar of this size.

3. If the bus bar were made of such size as to carry 500 amp. per square inch of area, what would be the annual cost of power loss, and what would be the difference in bus-bar investment cost per 1,000 ft. as compared with the size called for by Kelvin's law?

358. Owing to war conditions, silver bus bars were used in certain plants built in 1942 for production of aluminum and magnesium. Assume a current of 20,000 amp., length of 1,000 ft., and temperature of 40°C. Value of silver bus bar, $0.40 per ounce troy. Cost of power, $65 per kilowatt-year. Interest rate, 4 per cent.

Resistivity of silver = 1.629 microhms per centimeter cube at 20°C.

Temperature coefficient = 0.0038 per degree at 20°C.

For the corresponding data for copper, see Prob. 357.

Required: 1. The most economical size of silver bus bar, according to Kelvin's law.

2. The annual value of the power loss, and the saving in value of power loss as compared with a copper bus bar of the same size.

3. The value of the bus-bar investment for the silver and for the copper bus bars of the same size, assuming copper bus bars cost 18 cts. per pound.

4. The initial rate of temperature rise in the silver bus bar, in degrees Fahrenheit per minute.

359. A bare round copper conductor is 1 in. in diameter and carries a current of 1,000 amp. The temperature of the surroundings is 27°C.

Required: 1. If the surface of the conductor is bright ($E = 0.03$), what will be its working temperature?

2. The same, if the surface is oxidized ($E = 0.77$).

NOTE: For convection, take $B = 0.58$. $S = 2.4$.

360. A conductor is desired to carry 4,000 amp. a distance of 300 meters. Round copper bars cost $0.19 per pound. Conductivity of copper, 580,000 reciprocal ohms per centimeter cube. Round aluminum conductors cost $0.22 per pound; conductivity, 372,000. Cost of electric power as delivered, $75 per kilowatt-year. Average temperature of air, 20°C.; air assumed still. Interest rate, 5 per cent per annum.

Required: 1. The cross-sectional area of copper conductor that will give a minimum cost of power plus interest on the investment.

2. The same, for aluminum.

3. The initial rate of rise in temperature of the copper bars above room temperature, as calculated from the heat capacity.

4. The same, for aluminum.

5. The final working temperature for the copper and for the aluminum, taking radiation and convection into account. (For radiation, assume $E = 0.77$ for copper and 0.10 for aluminum. For convection, assume $S = 0.13$ for copper and 0.10 for aluminum. $B = 0.58$.)

CHAPTER XXII

DISTILLATION PROCESSES

Distillation is regularly applied for extracting zinc and mercury from ores and also has a number of other applications in metallurgy. In the typical process, as used for zinc and mercury, the metal is reduced directly in the form of vapor; the vapor is then passed into a condenser, where it condenses to liquid as it cools. Although the formation of the metallic vapor takes place simultaneously with reduction, a study of the process requires that the two actions be considered separately, and also the relation of one to the other.

Distillation of Zinc.—The reduction of zinc in the retort is usually considered as being governed by the reaction

$$ZnO + C = Zn + CO. \qquad (1)$$

Actually very little of the ZnO is directly reduced by solid carbon. Instead the reduction is chiefly by CO:

$$ZnO + CO = Zn + CO_2. \qquad (2)$$

Since CO_2 does not exist in the retort gases in a large percentage, most of it must be reduced to CO as rapidly as it is formed—practically simultaneously with its formation.[1] This reduction reaction is:

$$CO_2 + C = 2CO. \qquad (3)$$

This reaction constitutes the source of the CO needed in Eq. (2). It can take place to some extent before reaction (2) begins, thus producing the necessary concentration of CO; the presence of some air in the retort when it is charged will result in burning some carbon to CO_2, which is then reduced to CO as the charge heats; or there may be some direct combustion of C to CO. Equation (2) is reversible and will go from right to left, forming ZnO from metallic zinc (as indeed is purposely done in the French process of making ZnO) if CO_2 is present in sufficient concentration. But the presence of a considerable excess of carbon and of the CO formed in Eq. (3) counteracts this tendency and causes the reaction to take place chiefly in the left-right direction as desired.

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[1] The actual percentage of CO_2 in zinc-retort gases is probably larger than has generally been believed. It may reach several per cent without causing the reaction to be reversed.

Addition of Eqs. (2) and (3) yields Eq. (1), so that Eq. (1) truly represents the *result*, except in so far as it may be slightly disturbed by minor reactions. For example, whereas Eq. (1) requires that the gas coming out of the retort shall be 50 per cent CO and 50 per cent zinc vapor by volume, the ratio may at times be nearer 55:45. Some CO_2, H_2, and CH_4 may also be present, but for the purposes of study by calculation these departures from the ideal may often be ignored. Study of the mechanism of zinc reduction and of the equilibria involved requires that Eqs. (2) and (3) be considered separately, but for most other purposes, including thermal study, Eq. (1) may be used. Equation (1) is the result of Eqs. (2) and (3) with respect to heats of reaction just as much as with respect to weights of substances involved.

As the charge in the zinc retort is heated, at first no measurable reduction of ZnO occurs. Other actions, such as evaporation of moisture, expulsion of volatile matter from the coal, and reduction of chemically weaker elements (especially lead, iron, and cadmium), begin to be of importance first. Some of these are completed before an appreciable amount of zinc is reduced; others may overlap into the period of active zinc reduction.

The necessary minimum temperature for zinc reduction is that temperature at which the tendency for gas to form, as measured by its pressure, equals or exceeds the opposing pressure. If the retort were partly evacuated, the reaction would begin at a lower temperature; if it were put under pressure, a higher temperature would be required. For continuous reduction in a retort with only a small opening, the combined pressure of the gases formed (mostly Zn + CO) must equal or exceed the atmospheric pressure.

At any given pressure in a nearly closed retort, there is a temperature below which zinc will not be reduced (except in an inappreciable amount) and above which the reduction reaction will proceed continuously. This "reduction temperature" does not vary for different roasted ores; it is the same for all ores in which the zinc is being reduced from uncombined ZnO. When the pressure is normal atmospheric pressure, 760 mm., this temperature is called the "normal reduction temperature." Just above the reduction temperature, the *rate* at which reduction proceeds is relatively low, the reaction velocity increasing as the temperature is raised.

At the normal reduction temperature the pressure of the gases resulting from the reduction totals 760 mm. At this temperature reduction will proceed continuously in a retort or other vessel open to the atmosphere (at 760 mm.), even though the opening be small and such as to preclude the carrying away of the gases by a draft. At this temperature the gases are formed and automatically expelled against normal opposing pressure, by their own reaction pressure. The locus of this temperature is in many respects analogous to the locus of the normal boiling point.

The normal reduction temperature of zinc oxide by carbon has been determined accurately by Maier as 857°C.

On an open hearth with a draft to carry off the products of the reaction, reduction could proceed at lower temperatures, but the amount of reduction would become inappreciable with a moderate fall of temperature, probably above a low red heat. The amount of reduction in a given time would be severely limited by a low reaction rate as well as by a low reaction pressure.

The normal boiling point of zinc is 905°C., this being the temperature at which the vapor pressure of zinc is 760 mm. But the zinc reduced in the retort will be vaporized at a temperature even lower than this, because zinc vapor forms only part of the gas in the retort and therefore its pressure is only part of the total pressure in the retort. Zinc will be vaporized when the vapor pressure of the zinc equals or exceeds the pressure of the *zinc vapor* opposing. Since the gases are approximately 50 per cent zinc vapor, this pressure is approximately one-half of 760, or 380 mm. The minimum temperature at which the zinc will form in the retort as vapor is therefore calculated from the vapor-pressure formula for zinc,

$$\log p = -\frac{6{,}163}{T} + 8.108, \tag{4}$$

380 being used for the value of p. From this, T is found to be 1115°K., or $t = 842°C$. In this manner the temperature is readily determined for any value of p.*

Since the minimum temperature for continuous reduction of zinc in the retort at atmospheric pressure, about 857°C., is above the vaporization temperature as just calculated, all the zinc must form as vapor. But if the retort were sealed and the pressure raised, the vaporization temperature would be raised and thus the zinc might form as liquid. But, at the same time, the increase of pressure raises the reduction temperature, so that it requires a simultaneous solution of the equations of reduction and vaporization to determine whether zinc can form as liquid and, if so, at what temperature and pressure. The equation for the temperature-pressure relation in reduction can be determined approximately in accordance with the discussion on page 360 and the illustration there given.

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* The more precise formula

$$\log p = -\frac{6{,}634}{T} - 1.203 \log T + 12.184$$

may be used but entails difficulty in solving for T. The solution for T is best made by trial of different values of T. This gives $T = 1120°K.$, $t = 847°C$.

Condensation of the Zinc Vapor.—The mixture of CO and zinc vapor formed in the retort is discharged into a fire-clay condenser attached directly to the mouth of the retort and projecting into the air outside the furnace. As the mixture cools in the condenser, it soon reaches a temperature where the 380 mm. pressure of the zinc vapor represents saturation—the temperature found above by substituting 380 for p in Eq. (4). As the temperature falls below this saturation point, zinc vapor must condense to liquid zinc; and the lower the temperature falls, the greater the proportion of the zinc that condenses. Absolutely complete condensation of the vapor would require the temperature of absolute zero, but practically complete condensation is attained at fairly high temperature. In practice the gases leave the condenser and escape into the air (or into prolongs in some foreign plants) at a temperature that must be low enough to condense nearly all the zinc but must still be well above the freezing point of the metal. If the temperature of the escaping gases is known, the proportion of the zinc escaping condensation can be calculated.

Suppose, for example, that the temperature of the gases as they leave the condenser is 500°C. From the log p formula, it is found that the vapor tension of zinc at 500° is 1.3 mm. Suppose that the barometric pressure is 740 mm. It is then readily shown that the proportion of the zinc vapor escaping condensation (assuming that the gases were originally 50 per cent zinc vapor) is $\frac{1.3}{740 - 1.3}$, or 0.18 per cent. Evidently it is desirable that the gases be cooled to or below 500°C.

Condensation in the Production of Mercury.—Rather than to set down the steps by which the above result is obtained, it will be better to make the solution of the problem more general. The proportion of vapor escaping condensation is given by the expression $\frac{p}{P - p}$ (as used above) only when the vapor constituted 50 per cent of the gases before condensation began. The solution should be applicable, not only to any temperature and barometric pressure, but also to a gas mixture containing any percentage of vapor and to a mixture containing two or more condensable vapors, with determination of the percentage of *each* remaining uncondensed. The solution can be worked out with algebraic symbols, giving a formula for the desired result; but since the use of a formula would obscure the important principles involved—principles which require some thought for full understanding—the development of a formula will not be performed here but will be left for the student if desired. Instead, an illustration of the more general solution will be given from practical data, using condensation in the metallurgy of mercury, where the gases contain water vapor as well as mercury vapor.

Example 42

A mercury ore is treated by roasting and passing the gases into condensers. The gases entering the condensers have the following analysis:

	Per Cent		Per Cent
Hg	0 3	CO_2	30 7
SO_2	0.4	H_2O	20 1
O_2	3 5	N_2	45 0

The gases leave the condensers at a temperature of 55°C. Barometer, 750 mm.

Required: 1. The temperature at which the Hg and the H_2O will begin to condense

2. The percentages of the entering Hg and H_2O which remain uncondensed in the exit gases.

Solution: The partial pressure of the water vapor in the gases is $0.201 \times 750 = 151$ mm. From Table XXIV, page 401, it is seen that this is the saturation pressure at approximately 60°C. (1).

The partial pressure of the mercury vapor is $0.003 \times 750 = 2.25$ mm. Substituting this value for p in the expression for the vapor pressure of mercury:

$$\log p = -\frac{3,066}{T} + 7.752.$$

Solving for T, $T = 415$°K., or $t = 142$°C.*

Therefore, the mercury will begin to condense at 142°C. and the water at 60°C. (1).

The percentage of the mercury remaining uncondensed will be given by:

$$\frac{\text{amount of Hg leaving the condenser}}{\text{amount of Hg entering the condenser}}$$

The denominator, the amount of Hg entering, is 0.3 per cent of the total gas; but, in order to calculate the result desired, it will be necessary to know this amount, not in terms of the total gas, but in terms of that portion of the gas which remains unchanged during the process of condensation—*i.e.*, in terms of the noncondensable gas—so that the numerator may be expressed in the same terms and the percentage obtained In other words, since the numerator is based on gas *leaving* and the denominator on gas *entering*, each must be expressed in terms of a quantity that is the same on leaving as on entering For this reference quantity we take the volume of the noncondensable gas, referred to standard conditions. (The actual volume, of course, shrinks as the gases cool, but this contraction applies equally to all the gases present and does not affect the problem; the volume referred to standard conditions does not change for the noncondensable gas)

Call the volume of noncondensable gas V. (It may be preferred to call it 1, or 22.4, or some other value; any designation may be used, as the quantity will cancel out.) Then the percentage of noncondensable gas in the gases entering is $100 - 0\ 3 - 20.1$, or 79.6 per cent. Then the volume of mercury vapor entering is $\frac{0.003}{0.796} V$, or $0.00377V$.

The volume of mercury vapor leaving is (from Dalton's law) equal to $\frac{p_1}{p_2} V$, where p_1 is the partial pressure of the mercury vapor and p_2 the partial pressure of the noncondensable gases when leaving. The partial pressure of the mercury vapor may be found by substituting (55 + 273) for T in the expression

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* It would be a little more accurate to refer to the table, similar to the one for water, giving actual measurements of the vapor pressure of mercury. The temperature corresponding to 2.25 mm. in this table is 144°C. (See Table XXV, p. 402)

$$\log p = -\frac{3{,}066}{T} + 7.752,$$

whence $p = 0.025$ mm.

The partial pressure of the water vapor leaving is found by looking up the pressure corresponding to 55°C. in Table XXIV, page 401. This is 118 mm. Hence the partial pressure of the noncondensable gases, p_0, is $750 - 0.025 - 118 = 632$ mm. Therefore the volume of mercury vapor leaving is $\frac{0.025}{632}V$, or $0.000040V$.

The percentage of the mercury vapor remaining uncondensed is therefore $\frac{0.000040V}{0.00377V} = 1.1$ per cent (2).

The volume of water vapor entering is $\frac{0.201}{0.796}V$, or $0.253V$. The volume of water vapor leaving is $^{118}/_{632}V$, or $0.187V$. The percentage of the water vapor remaining uncondensed is therefore $\frac{0.187V}{0.253V} = 74.0$ per cent (2).

NOTE: The volumes entering have been calculated from the percentage composition as given. These could equally well have been calculated from the partial pressures (obtained in requirement 1), just as was done with the volumes leaving.

Production of Zinc Oxide.—A number of zinc-reduction plants produce zinc oxide as well as metallic zinc. In the Wetherill, or American, process, which is most commonly employed, the oxide is made directly from roasted ore. The oxide production consists essentially of two stages, of which the first is chemically the same as in producing metallic zinc, *viz.*, reduction of ZnO in the ore by carbon in the form of coal mixed with the charge, the zinc being formed as vapor. Instead of being carried on in a retort, the action takes place on a hearth or a traveling grate. In the second stage the zinc vapor is immediately reoxidized by excess air or CO_2. The resulting oxide is carried to a baghouse as a fume suspended in the furnace gases. CO formed in the first stage is subsequently oxidized to CO_2.

Because of the similarity of the first stage to the production of metallic zinc, two problems on the Wetherill process are included in this chapter.

Problems

361. An ore containing 36 per cent Zn in the form of the sulphide ZnS is roasted until it has only 2 per cent ZnS:

$$2ZnS + 3O_2 = 2ZnO + 2SO_2$$

The roasted product is mixed with coal and treated in a retort furnace, 6 per cent of the ZnO remaining unreduced.

$$ZnO + C = Zn + CO.$$

Required: 1. The volume and weight of air used for the roasting of 1 metric ton of ore, allowing 20 per cent excess over the theoretical requirement and assuming no fuel necessary.

2. The percentage composition of the gases from the roasting furnace, assuming them to contain only N_2, O_2, and SO_2.

3. The weight of zinc produced from 1 ton of ore.

4. The percentage composition of the gas issuing from the retorts, both by weight and by volume.

362. A roasted zinc ore had the following composition:

	Per Cent		Per Cent
ZnO	66	Fe_2O_3	14
ZnS	3	Al_2O_3	1
PbO	10	SiO_2	6

The ore was treated in a horizontal retort, the charge consisting of 100 lb. of ore mixed with 45 lb. of coal. Assume that the coal was 90 per cent C, 10 per cent SiO_2 In the retort, 91 per cent of the ZnO was reduced to metal, together with all the PbO Three-fourths of the Fe_2O_3 was reduced to Fe and one-fourth to FeO. Assume that zinc was reduced by the reaction $ZnO + C = Zn + CO$.

Required: 1. The weight of zinc reduced, and the percentage extraction of zinc from the ore.

2. The percentage excess carbon in the charge over the theoretical requirement of carbon for reduction of all the ZnO.

3. The weight and percentage composition of the residue in the retort after elimination of the zinc vapor (Neglect vaporization of lead and iron, and assume no reoxidation of these elements.)

363. The charge placed in a zinc retort contains 45 per cent ZnO, 20 gangue and coal ash (assume pure SiO_2), and 35 carbon. Assume that reduction takes place according to the reaction

$$ZnO + C = Zn(g) + CO.$$

This reduction begins when the temperature has reached 860°C., but the temperature inside the retort during active distillation is 1250°C.

The charge weighs 120 lb , and 90 per cent of its zinc content is reduced and recovered.

Required· 1. The heat (in pound-calories) required to heat the entire charge from 0 to 860°C.

2. The heat of the reaction as it proceeds at the temperature of 1250°C. during active distillation

3 The total heat required per pound of zinc recovered, starting with cold charge and discharging the products (including the retort residue) at an average temperature of 1250°C.

4. The pounds of coal needed to supply this heat (per pound of zinc) at the average thermal efficiency of 15 per cent; also the total coal consumption (per pound of zinc recovered), including that used in the retort. (Assume coal to be 90 per cent carbon, 10 per cent SiO_2.)

364. Assume that the reduction in a zinc retort takes place according to the equation

$$ZnO + C = Zn + CO.$$

Assume that the mixture charged into the retort is 48 per cent ZnO, together with three times the theoretical amount of carbon, and the balance gangue plus coal ash, which may be counted as SiO_2.

Assume that the reduction takes place at 1000°C. The gases leave the retort at 1300°C.

Required: Per 65.4 kg. of zinc reduced:

1. The heat of the reaction, starting and ending cold.

2. The heat of the reaction as it takes place at 1000°C.

3. The heat theoretically absorbed in reduction, starting cold and ending with the products at 1000°C.

4. The additional heat required to deliver the gases at 1300°.

5. The actual heat required for the charge, starting with cold charge and ending with gases and residue both at 1300°C.

6. How many kilograms of coal having a calorific power of 6,500 would be required per kilogram of zinc to supply this heat (as in 5) at a thermal efficiency of 10 per cent?

7. If the reduction were carried out in an electric furnace at 50 per cent electrothermal efficiency, how many kilowatt-hours would be consumed per kilogram of zinc?

365. Zinc is reduced in a retort according to the following reaction:

$$ZnO + C = Zn + CO.$$

The products enter the condenser at 1000°C., and the uncondensed portion leaves the condenser at 420°C.

Required: 1 As the vapor cools in the condenser, at what temperature will the zinc begin to condense?

2. What percentage of the zinc is lost as uncondensed vapor?

366. Assume that the gases passing out of a zinc retort consist volumetrically of:

	Per Cent
Zn	40
CO	56
CO_2	2
N_2	2

They pass into the condenser at an average temperature of 1000°C. and leave the condenser at 450°C.

Required: 1. Per kilogram of zinc leaving the retort, the amount of heat in the gases, calculated to 0°C. as a base line.

2 Per kilogram of zinc leaving the retort, what weight of zinc is carried out of the condenser as vapor?

3. Per kilogram of zinc leaving the retort, how much heat is carried out of the condenser by the gases, and how much is dropped in the condenser?

4. At what temperature of the gases, in the condenser, will zinc begin to condense?

5. What temperature must be reached in the condenser in order that 99 per cent of the zinc may be condensed?

6. If the condenser is made of fire clay having a resistivity of 80 thermal ohms per centimeter cube and the mean area of its wall 0.4 sq. m., what must be the average outside temperature to disperse the heat dropped in it? Assume 4 kg. of zinc made per hour, with wall thickness of 3.5 cm.

367. A charge of zinc ore in a zinc retort gives off gas which analyzes:

	Per Cent
Zn	37.0
CO	55 0
H_2	4.75
CO_2	3.0
Pb	0 25

It passes into the condenser at 1200°C., and the gas issuing from the condenser is at 625°C. Barometer, 760 mm.

Required: 1. The partial pressures sustained by the zinc and the lead vapors, at 1200° and 760 mm. pressure.

2. The proportion of the zinc entering the condenser lost in the escaping gas as zinc vapor.

3. The proportion of the lead vapor entering the condensers which escapes.

4. The same proportions (requirements 2 and 3) if the zinc works is operating at 2,000 m. above sea level (barometric pressure, 591 mm.).

368. The gases formed in reduction in a zinc retort of the continuous vertical type contain 48 per cent zinc vapor, 0.3 cadmium, 0.5 lead, and the balance noncondensable gases (chiefly CO). These pass into a condenser having a "deleading" section. The pressure in the condenser is 745 mm.

Required: 1. The temperatures at which condensation of the lead, zinc, and cadmium will begin.

2. The percentage of the lead content that would be condensed before condensation of zinc begins, assuming sufficient time for the condensation.

3. The percentage of the zinc content that would be condensed before condensation of cadmium begins, assuming sufficient time for the condensation.

369. In a zinc works using prolongs, the gases issuing from the retort had the following analysis, by volume:

	Per Cent
Zn	44
CO	54
Cd	0 6
Pb	0 2
CO_2	1 2

The temperatures were as follows:

Leaving the retort and entering the condenser,	1250°C.
Leaving the condenser and entering the prolong,	520°C
Leaving the prolong,	380°C.

The total pressure was 740 mm., approximately uniform in all parts of the system

Required: Of the amounts of zinc, cadmium, and lead (each) issuing from the retort, what percentages are:

1. Recovered in the condenser?
2. Recovered in the prolong?
3. Lost, passing out of the prolong uncondensed?

370. 1. The net reaction for the reduction of zinc oxide is:

$$ZnO + C = Zn + CO.$$

What is the heat of the reaction at 950°C.?

2. What is the total heat absorption per kilogram of zinc produced, to turn out the retort gases at 1200°C.?

3. At what temperature will the zinc in the issuing gases begin to condense, and at what temperature will it be 99 per cent condensed?

4. How much pressure would have to be applied to the retort to obtain the zinc in the liquid condition (at 1200°C.) instead of as vapor?

371. A charge of 50 kg. of zinc ore is treated in a fire-clay retort 140 cm. long and 60 cm. in circumference, these being mean values measured between the inside and outside of the walls of the retort. It may be assumed that the mean areas may be calculated directly from these dimensions in the simple geometrical formulas. Assume that the retorts receive heat through the sides and one end.

It requires 6 hr. after reduction commences to complete driving off the zinc, and the total heat absorbed in reduction of the charge is 36,500 Cal. The average temperature in the interior of the retort is 1200°C., while the temperature of the outside of the retorts is 1350°C. The walls are 3 cm. thick.

The gases issuing from the retort are 58 per cent CO, 42 per cent zinc vapor. They enter the condenser at 1000°C., and the uncondensed portion leaves the condenser at 440°C. Barometer, 760 mm.

Required: 1. The thermal conductivity of the fire clay at the operating temperature, in reciprocal thermal ohms (watts per degree) per centimeter cube.

2. As the gases cool in the condenser, at what temperature will the zinc begin to condense?

3. What percentage of the zinc is lost in the uncondensed gases leaving the condenser?

372. Eulenstein gives the following data for the running of a Siemens regenerative gas muffle furnace reducing roasted zinc ore:

Ore treated per day (gangue SiO_2)	5,000 kg.,	51.74 per cent Zn as ZnO
Skimmings returned	320 kg.,	49.5 per cent Zn as ZnO
Products:		
Zinc	2,117 kg ,	100 per cent Zn
Blue powder	200 kg ,	80 per cent Zn
Reduction coal, 10 per cent H_2O, 90 per cent C	2,100 kg	
Gas used	21,465 cu. m.	
Moisture with gas	1,524 kg.	

Gas composition:

	Per Cent
CO_2	5.7
O_2	0.2
CO	22.1
CH_4	4.2
H_2	8.8
N_2	59.0

The gas reaches the furnace at 765°C. The air used is at 900°C Gases leave furnace at 1200°C.

Required: 1. A heat balance of the furnace, per 1,000 kg. of ore treated, showing.

a. Heat in hot gas and air used.
b. Heat generated by its combustion.
c. Heat carried out by gases at 1200°.
d Heat in condenser vapor and gases at 1000°.
e. Heat absorbed in chemical reactions in retorts.
f. Heat in retort residues, discharged at 1200°.
g. Heat lost by conduction and radiation.

2. The net thermal efficiency of the furnace

373. In the Wetherill process the furnace first receives a charge of "bed coal." After 20 to 30 min. this has heated the furnace to about 1200°C. The main charge of roasted ore mixed with coal is then put in, being charged cold.

Three distinct reactions occur, as follows: (1) reduction of zinc oxide by carbon, (2) reoxidation of zinc vapor to zinc oxide, and (3) oxidation of CO to CO_2.

Required: 1. The heat generated or required (which?) by reaction 1, the reagents being cold and the products at 1200°C.

2. The same for reaction 2, the reagents and products being at 1200°C., except the oxygen, which enters cold.

3. The same for reaction 3, the conditions being the same as in requirement 2.

4. The net heat liberated or absorbed (which?) by the three reactions combined, per kilogram of ZnO produced

5. How much additional heat (per kilogram of zinc oxide) will be required because the air enters at 0° and the residual nitrogen and excess air leave at 1200°, assuming 100 per cent excess air used?

374. The following data apply to the Wetherill process as used on franklinite ore by the New Jersey Zinc Co.:

Ore, per cent	Residue, per cent	Coal, per cent
Zn 18.2	Zn 4.8	C 88
Fe 35.0	Fe 40.0	Ash 12
Mn 12.8	Mn 14.6	
SiO_2 3.6		
CaO 7.0		

The iron in the ore is Fe_2O_3; in the residue, FeO. The charge to the furnace is 1,800 lb. of ore and 900 lb. of coal; this is preceded by an ignition charge of 250 lb of coal. The oxide made carries 99.5 per cent ZnO. The residue is smelted in a blast furnace to spiegeleisen in which the Fe:Mn ratio is 4:1. There is 5 per cent C in the spiegel, and 10 per cent loss of manganese in smelting. The Zn in the residue is recovered from the furnace gases as impure oxide, 95 per cent ZnO.

Required: 1. The weight of residue made, per charge, and per ton of ore.

2. The recovery of oxide, per ton of ore, and the percentage of the zinc of the ore recovered as pure oxide

3. The amount of unburned carbon left in the residue.

4. The amount of coal used, per ton of ore.

5. How much iron ore (80 per cent Fe_2O_3) can be added in the blast furnace, per ton of residue?

6. The amount of impure oxide recovered from the blast-furnace gases, per ton of residue.

375. A mercury ore is treated by roasting and passing the gases into condensers. The gases entering the condensers have the following analysis:

	Per Cent		Per Cent
Hg	0.3	CO_2	22.7
SO_2	0.4	H_2O	28.1
O_2	3.5	N_2	45.0

The gases enter the condensers at a temperature of 600°C. and leave at 65°C. Barometer, 760 mm.

The average temperature of the condensed liquid mercury and water in the condensers is 70°C.

Required: 1. The partial pressure of the Hg and of the H_2O in the entering gases, in millimeters of Hg.

2. The temperature at which the Hg and the H_2O will begin to condense.

3. The partial pressure of the Hg and of the H_2O in the exit gases, in millimeters of Hg.

4. The percentages of the entering Hg and H_2O that remain uncondensed in the exit gases

5. The total amount of heat given up in the condenser, per kilogram of mercury entering the condenser.

376. Mercury is extracted from an ore by roasting and passing the gases into condensers. The gases enter the condensers at 650°C. and leave at 50°C. The composition of the entering gases is as follows:

	Per Cent		Per Cent
Hg	0.25	CO_2	29.6
SO_2	0.45	N_2	48.8
O_2	4.1	H_2O	16.8

The barometer is at 730 mm.

The Emmett mercury boiler installed at Hartford, Conn., is designed to evaporate 230,000 lb. of mercury per hour and superheats the vapor to 434°C. The vapor expands in a turbine, cooling to 212°C.

Required: 1. The partial pressure of Hg and of H_2O in the gases entering the condensers

2. The temperature at which the Hg and the H_2O will begin to condense.

3. The percentage of the entering Hg and H_2O that remains uncondensed in the gases leaving the condensers.

4. The pressure exerted by the Hg in expansion in the Emmett turbine, measured in millimeters and in pounds per square inch.

377. A mercury ore contains 2 per cent HgS; the gangue is $CaCO_3$, 80 per cent; SiO_2, 14; H_2O, 4.

The ore is roasted in rotary kilns, using 15 per cent of its weight of wood as fuel. Composition: cellulose ($C_6H_{10}O_5$), 70 per cent; H_2O, 30 per cent. Assume air used dry, at 0°C. Air used 20 per cent in excess of the theoretical amount

The gases enter the condensers at 600°C. and leave the condensers at 60°C.

Required: 1. The percentage composition of the gases produced.

2. The partial pressure of the mercury vapor and of the water vapor in the gases entering and leaving the condensers.

3. The temperature at which mercury will commence to condense.

4. The temperature at which H_2O will commence to condense

5. The percentage of the total mercury condensed before water commences to deposit.

6. The percentage of the total mercury escaping as vapor in the gases.

7. The percentage of the total water escaping as vapor in the gases.

378. Given the mercury ore and conditions of Prob. 377.

Required: Per ton of ore:

1 A heat balance of the rotary kiln.

2. A heat balance of the condenser.

CHAPTER XXIII

VAPOR PRESSURE AND TEMPERATURE-PRESSURE RELATIONS IN CHEMICAL REACTIONS

Chemical reactions resulting in the formation of gas are of frequent occurrence in metallurgy. This chapter will deal with those cases where a chemical change or the physical change of evaporation results in the formation of a gas from one or more solids or liquids.

Examples of reactions of this kind are:

$$ZnO + C \leftrightarrows Zn + CO.$$
$$FeCO_3 \leftrightarrows FeO + CO_2.$$
$$CuSO_4 \leftrightarrows CuO + SO_3.$$
$$PbS + 2PbO \leftrightarrows 3Pb + SO_2.$$
$$H_2O\ (l) \leftrightarrows H_2O\ (g).$$
$$Ag\ (l) \leftrightarrows Ag\ (g).$$

All these reactions when taking place from left to right represent an increase of volume, and all are reversible. Each also is governed by a condition of equilibrium such that the reaction cannot move from left to right unless the pressure of the gas or gases forming equals or exceeds the opposing partial pressure of the same gas or gases already formed. When equilibrium has been established under a set of conditions of temperature, pressure, and volume, a change in any one of the conditions destroys the equilibrium and causes the reaction to go in one direction or the other. When they take place from left to right under the usual conditions of constant pressure, the total energy change involved includes the doing of mechanical work equal to $p\Delta v$, the product of the volume change times the opposing pressure; this portion is in general relatively small.

The last two equations above represent simply the evaporation of water and of molten silver. It is obvious that this action is similar in many respects to the chemical reactions, and the remarks made above apply equally to these and to the other equations. The process of evaporation will be used as the basis of the discussion following, and later the application to chemical reactions will be taken up.

VAPOR PRESSURE AND ITS RELATION TO TEMPERATURE

The vapor pressure[1] of a substance at a given temperature is a measure of its tendency to vaporize at that temperature. Frequent use of high temperatures and also of distillation processes makes this question an important one in metallurgy.

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[1] The terms "vapor tension" and "vapor pressure" are used interchangeably.

The relation between the temperature and the vapor pressure can be expressed most simply, though not with complete accuracy, in the form of the relation

$$\log p = -\frac{A}{T} + B,$$

in which p is the vapor pressure, T is the temperature on the absolute scale, and A and B are constants. Values of A and B for the important metals and other elements are given in Table XXII, page 399. When these values are used, $\log p$ is the common logarithm of p expressed in millimeters of mercury, and T is expressed in degrees Kelvin. With some of the elements over limited ranges the values of A and B are known with considerable accuracy; but in the case of many elements the values are somewhat questionable, and the reliability of results from their use is also diminished when they are used outside the temperature range indicated in the table.

Use of the above formula accordingly affords a simple means of finding the vapor pressure of an element at a given temperature, with varying degrees of accuracy. Before proceeding with applications of the formula, however, it will be highly desirable to discuss the important principles involved in the derivation of the formula, as well as the general variation of vapor pressure with temperature.

Vapor-pressure-temperature Curves.—The study of actual vapor pressures begins with experimental measurement of the vapor pressures of substances having low boiling points, such as alcohol, water, iodine, and mercury. In Fig. 15 are shown curves of the vapor pressures of water and mercury as measured, plotted against temperature.[1] It is found that the shape of these curves is characteristic of the vapor pressures of substances. Indeed, a method that has been used considerably of estimating the vapor pressure of a metal is given by the rule that the absolute temperatures at which the given metal and mercury have the same vapor pressure stand approximately in a fixed ratio. For mercury and water, for example, this ratio is about 1.7:1, and for lead and mercury about 3.1:1. Thus, knowing that the vapor pressure of mercury is 17 mm. at 200°C., it could be estimated that the vapor pressure of lead would be 17 mm. at about $3.1 \times 473 = 1466$°K., or 1193°C. This rule, however, is not sufficiently accurate for most purposes.

If the temperature be plotted against $\log p$ instead of against p, the graph is more nearly straight, and the curve bends in the opposite direction from those in Fig. 15. The curve has the form of the graph of the equation $x = \frac{1}{y} + c$.

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[1] The data for these curves are found in Tables XXIV and XXV, pp. 401 and 402.

If log p be plotted against $\frac{1}{T}$, the graph is a straight line ($x = y + c$). when the values of log p and $\frac{1}{T}$ are taken from the equation $\log p = -\frac{A}{T} + B$. When the values are taken from actual observed data, the graph departs slightly from a straight line, and the departure shows that actually the vapor tension of the element cannot be exactly expressed by the equation $\log p = -\frac{A}{T} + B$. This is indeed the case, as will be noted further on. In Fig. 16 the logarithms of the values used in Fig. 15 for water and mercury are plotted against $\frac{1}{T}$. The corresponding lines for zinc, lead, silver, and copper as obtained from the values of A and B

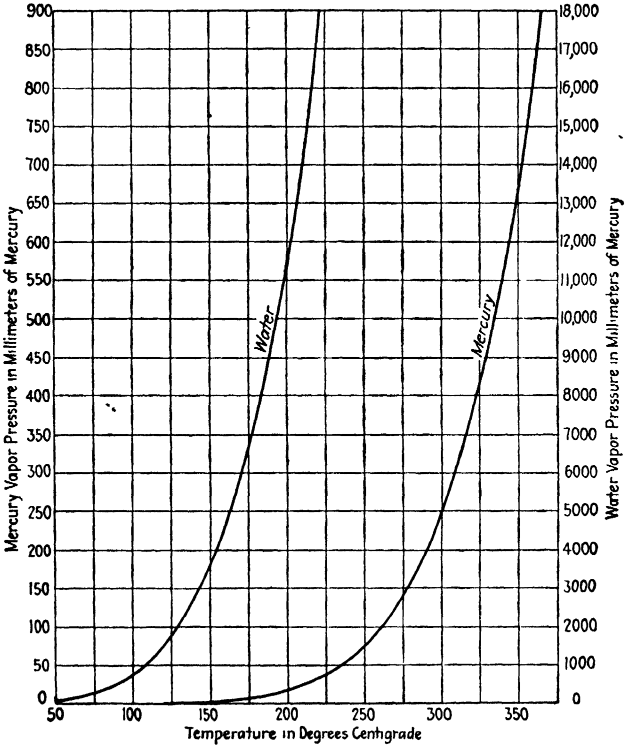

FIG. 15.—Variation of vapor pressure with temperature.

given in Table XXII, page 399 are also shown. It is seen that there is a slight curvature in the lines for water and mercury.

Meaning of the Quantity A.—The value of A in the vapor-pressure formula is given by the relation $A = \frac{\Lambda}{4.578}$, in which Λ is the latent heat of vaporization of the substance in calories per mol. This interesting relation enables one to derive the value of A when the heat of vaporization is known, and vice versa; and when both the heat of vaporization and the normal boiling point are known, it is possible to obtain the values of both A and B in the vapor-pressure formula.

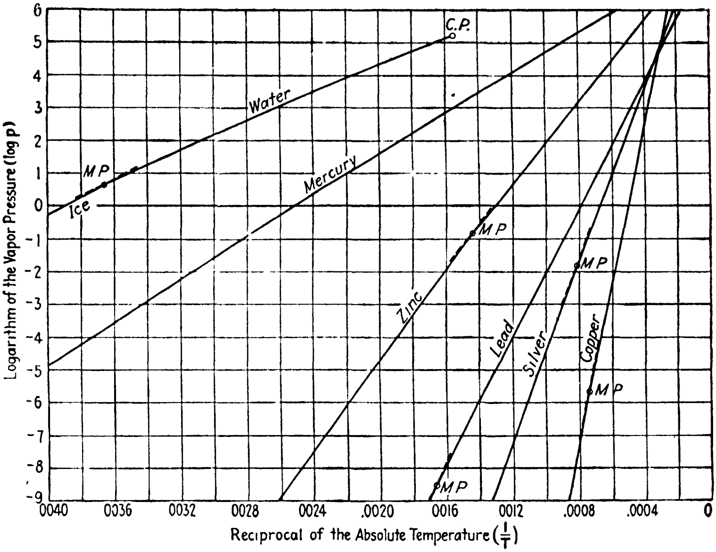

FIG 16.—Logarithm of the vapor pressure of various substances plotted against the reciprocal of the absolute temperature.

Meaning of the Quantity B.—It may be noted that B is the value of $\log p$ when $T = \infty$: *i.e.*, as T becomes infinite in this equation, $\log p$ approaches the value B, suggesting a limiting value for the vapor pressure. This interpretation of the value of B, however, is not borne out in the more accurate expression of the vapor-pressure curve [Eq. (5), page 349], and hence must be abandoned. B is a constant of integration, the evaluation of which is different in different instances.

Calculation of the Value of B from the Value of A and the Normal Boiling Point.—As an example of this calculation, the heat of vaporization of cadmium is 212 cal. per gram = 112.4 × 212 or 23,800 cal. per mol. Therefore, $A = \frac{23,800}{4.58} = 5,200$. Then $\log p = -\frac{5,200}{T} + B$ (1).

The boiling point of cadmium is 765°C.; therefore, when $T = 765 + 273$, $p = 760$. Substituting these values in Eq. (1), we find $B = 7.89$.

Instead of the normal boiling point, any known pair of values for p and T may be used.

Trouton's Rule.—An empirical rule first stated by Trouton in 1884 connects the molecular latent heat of vaporization with the absolute temperature of the normal boiling point, stating that the heat of vaporization per mol divided by the normal boiling temperature in degrees absolute is a constant for all liquids (except a certain class called "polar liquids," which includes water and fused salts):

$$\frac{\Lambda}{T} = c.$$

It is found that c is only roughly constant for different substances. Its value is usually considered as about 21, but for most metals it is about 23. It tends to be higher for substances having higher boiling points.

It may be noted that c is in reality the increase of entropy in vaporization. As such it may be denoted by ΔS.

Application of Trouton's Rule.—Trouton's rule may be expressed for most metals by the relation

$$\Lambda = 23T,$$

in which Λ is the heat of vaporization[1] in calories per mol and T is the normal boiling point in degrees Kelvin. Since this rule connects the heat of vaporization and the boiling point, the vapor-pressure constants may be estimated when *either one* of these quantities is known. However, the value for c in Trouton's rule is not sufficiently constant for different metals to provide a desirable degree of accuracy; hence, while this application is of much theoretical interest and may occasionally be of value in estimation, it is not generally reliable in practice.

Derivation of the Log *p* Equation.—Probably the first important study of the relation between vapor pressure and temperature was that of Clapeyron, who in 1834 derived the relation[2] that may be expressed:

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[1] "Heat of vaporization," often called "latent heat of vaporization," includes the heat corresponding to the external work done by increase of volume (accompanying formation of the vapor) against the surrounding pressure ($p\,\Delta V$) as well as the internal-energy change. This external work usually amounts to a few per cent of the total For example, in the vaporization of water at 100°C., the heat of vaporization is 539 Cal. per kilogram, of which 498 Cal. is the heat equivalent of internal work and 41 Cal. the heat equivalent of external work.

[2] This relation follows from the fundamental equation of the second law of thermodynamics:

$$A - Q = T\frac{dw}{dT},$$

in which A is the maximum work done in an isothermal process and Q is the decrease

$$\Lambda = T\frac{dp}{dT}\Delta V, \tag{1}$$

in which Λ is the heat of vaporization per mol and ΔV is the difference in volume between the mol of liquid and the mol of gas resulting. Since the volume of the liquid is relatively small, ΔV is practically the volume of the vapor, and if the vapor be regarded as a perfect gas, the gas-law equation may be applied. If the value of V from the equation

$$pV = RT \tag{2}$$

be substituted for ΔV in Eq. (1), then

$$\Lambda dT = RT^2\frac{dp}{p}, \text{ or } \frac{dp}{p} = \frac{\Lambda}{RT^2}dT. \tag{3}$$

When this equation is integrated, there follows the result:

$$\ln p = -\frac{\Lambda}{RT} + \text{const.} \tag{4}$$

Nernst considered the problem of the precise form of the vapor-pressure equation in much detail, both experimentally and mathematically, and reference should be made to his work.[1] He deduced an equation of the form:

$$\ln p = -\frac{\Lambda_0}{T} + a\log T - bT + c, \tag{5}$$

which gives accurately the shape of the vapor-pressure curve. But not only is this equation inconvenient to use in practice, but also the determination of the values of a, b, and c has been made for only a few substances. It seems best, therefore, to fall back on Eq. (4) as representing the curve with sufficient approximation and to consider the constant as a numerical one of which the value can be determined approximately by the method illustrated on page 347 (calculation of the value of B). In order to facilitate the use of Eq. (4), we change the logarithm to the base 10 and insert the numerical value of the gas constant R in gram-calorie units. We have then:

$$2.3026\log p = -\frac{\Lambda}{1.9885T} + \text{const.}$$

$$\log p = -\frac{\Lambda}{4.578T} + \text{const.}$$

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in total energy. The derivation is discussed by Clapeyron in *J. école polytech.*, **14**, 153 (1834).

[1] "Applications of Thermodynamics to Chemistry," Charles Scribner's Sons, New York, 1907, and elsewhere.

This may be written:

$$\log p = -\frac{A}{T} + B,$$

where

$$A = \frac{\Lambda}{4.578}. \tag{6}$$

In Eq. (5) Λ_0 is the heat of vaporization at 0°K., while in Eq. (6), Λ is the heat of vaporization at the temperature T. In deriving the numerical values of the constants A and B, Λ is usually taken at the normal boiling point. The variation in Λ at other temperatures, though small, is one of the reasons for the inaccuracy of the equation outside a limited range.

The derivation of the accurate form of the equation is based on free-energy change instead of heat of vaporization.

Determination of Constants *A* and *B* from Known Pairs of Values of *p* and *T*.—The formula

$$\log p = -\frac{A}{T} + B$$

has been used above to determine p for a given value of T or to determine T for a given value of p. The value of the constant A has been derived from the heat of vaporization and the value of B from a known pair of values of p and T, usually the normal boiling point.

This method may evidently be used in the reverse direction. That is, if any *two* pairs of values of p and T are known, these will give two simultaneous equations which may be solved to determine the values of A and B.

For example, the vapor pressure of mercury has been determined to be 247 mm. at 300°C. and 760 mm. at 357°C. (from Table XXV, page 402). We have then:

$$\log 247 = -\frac{A}{573} + B$$

and

$$\log 760 = -\frac{A}{630} + B.$$

Solving simultaneously, we find:

$$A = 3{,}090.$$
$$B = 7.786.$$

These values differ slightly from the values of A and B for mercury given in Table XXII, page 399, but a satisfactory degree of accuracy is indicated, the difference being well under 1 per cent.

Determination of the Heat of Vaporization from Measurements of Vapor Pressure.—The value of A having been determined from any two known pairs of values of vapor-pressure data, by the method just illustrated, this value of A substituted in the relation

$$\Lambda = 4.578A$$

gives the molal heat of vaporization.

Thus, for mercury, $\Lambda = 4.578 \times 3{,}090 = 14{,}150$ cal. per mol $= 70.5$ cal. per gram. Experimental measurements of this quantity have ranged from 68 to 70 cal. per gram.

THE VAPOR-PRESSURE FORMULA FOR SOLIDS (SUBLIMATION)

In the above formula, Λ represents the molal heat of vaporization of the liquid at the boiling point. At temperatures below the freezing point the substance is no longer a liquid, and the formula ceases to apply. There is a discontinuity in the vapor-pressure curve at the freezing point (see Fig. 16, page 347).

The transformation from solid to vapor represents two phase changes, solid to liquid and liquid to vapor. The energy absorbed may be regarded as made up of the heat of fusion plus the heat of vaporization. A formula of the same form as above,

$$\log p = -\frac{A'}{T} + B',$$

may be derived, in which the same general relations hold. $A' = \frac{\Lambda'}{4.578}$, where Λ' is the sum of the heats of fusion and vaporization.

A' having been determined, B' can then be determined in a manner similar to the determination of B already illustrated. A pair of values for p and T is required. Since at the melting point a substance may be partly solid and partly liquid, this point is common to the two curves: the value of T representing the melting point must give the same value for p, whether used in the formula for liquid or for solid. The pair of values needed can therefore be obtained from the formula for the liquid, the melting point being used for T.

The heat of vaporization employed for calculation of the vapor-pressure equation for the solid should be the heat of vaporization at the melting temperature, which differs slightly from the heat of vaporization at the boiling point used in the case of the liquid. It is not often necessary, however, to know the vapor pressure of the solid with great accuracy, since the values are usually extremely small; and accordingly this refinement may usually be omitted, as has been done in the following example. In fact, while the heat of vaporization at the melting point is always greater than the heat of vaporization at the boiling point, the difference between the two quantities is, in the case of most of the metals, less than the probable error in the stated value of either quantity in the present state of knowledge.

Example 43

Given the formula $\log p = -\frac{10,450}{T} + 8.876$ for the vapor pressure of molten bismuth, derive the constants in the similar formula for the vapor pressure of solid bismuth. Heat of fusion of bismuth = 12.0 cal. per gram. Atomic weight = 208.0. Melting point = 271°C.

Solution:

$$\Lambda = 4.578 \times 10,450 = 47,840 \text{ cal.}$$
$$\Lambda' = 47,840 + 208 \times 12.0 = 50,340 \text{ cal.}$$
$$A' = \frac{50,340}{4.578} = 11,000.$$

At 271°C., $\log p = -\frac{10,450}{544} + 8.876 = -10.334.$

This value must hold for either solid or liquid. Then:

$$-10.334 = -\frac{11,000}{544} + B'.$$
$$B' = 9.877.$$

The formula for the vapor pressure of solid bismuth is therefore:

$$\log p = -\frac{11,000}{T} + 9.877.$$

ACCURACY OF THE LOG p FORMULA FOR ZINC

Zinc is one of the few substances for which the vapor-pressure equation has been determined in the accurate form of Eq. (5), page 349. C. G. Maier[1] deduces the following equations and states that they may be used with confidence for any temperature up to 1500°C.:

For solid zinc:

$$\log p = -\frac{6,939.0}{T} - 0.1458 \log T - 0.0002883T + 9.7756.$$

For liquid zinc:

$$\log p = -\frac{6,789.5}{T} - 1.051 \log T - 0.0001255T + 12.0181.$$

The approximation equations, using the values for A and B given in Table XXII, page 399, are:

For solid zinc:

$$\log p = -\frac{6,950}{T} + 9.200.$$

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[1] "Zinc Smelting from a Chemical and Thermodynamic Viewpoint," *U. S. Bur. Mines, Bull.* 324, 1930.

For liquid zinc:

$$\log p = -\frac{6{,}163}{T} + 8.108.$$

To examine the accuracy of the approximation equation in this case, the following table is given showing the comparative values as obtained from the above two sets of equations over an extreme range of temperature:

Table VI.—Vapor Pressure of Zinc

Temperature, °C.	Vapor pressure, millimeters	
	From accurate equation	From approximation equation
25	1.13×10^{-14}	0.77×10^{-14}
200	3.82×10^{-6}	3.25×10^{-6}
600	11 00	11 2
900	720 2	715
1000	1,829	1,850
1200	7,842	8,400
1500	35,646	42,800

Vapor Pressure of Alloys

The vapor pressure of an alloy is an important factor both in making alloys containing an element of low boiling point (such as brass) and in applying the process of distillation to a mixture of metals or a metal containing impurities (as in distillation of zinc crusts in the Parkes process or in retorting of amalgam in the amalgamation process) or to an ore containing several elements that may vaporize in appreciable amounts.

A molten alloy is a liquid solution, and principles that apply to the vapor pressures of solutions must accordingly be considered in connection with alloys. The vapor pressure of an alloy will be governed in part by a law analogous to Dalton's law of partial pressures, thus: **The total vapor pressure of an alloy is equal to the sum of the *partial* vapor pressures of its constituents.** But the partial pressure of each component of the alloy is *lower* than the normal vapor pressure which the element would exert if it were not contained in an alloy.

The partial vapor pressure of the constituents will depend on the form in which the constituents exist in the alloy relative to each other, *i.e.*, whether they exist in chemical combination with each other, or simply as solutions, or as separate elements.

The simplest case occurs when the constituents occur as separate elements. Obviously this cannot occur with a liquid alloy, since then the elements are in solution.

When the elements are entirely distinct and separate, each may exert its own vapor pressure as though the other were not present. In the case of a closed vessel there would obviously be a limitation to this general statement, but even then it holds approximately up to some high pressure.

When, however, the elements are in solution with each other, whether solid or liquid, the vapor pressure of each is lowered. The following rule may then be applied: **The partial vapor pressure of an element in an alloy in which there is no heat of combination between the components is equal to the vapor pressure of the pure element multiplied by the mol-fraction of the element contained in the alloy.**

When the atom is identical with the molecule, as usually in the case of metals, the "mol-fraction" is identical with the "atom-fraction," or atomic per cent expressed as a fraction. "Atomic per cent" is the percentage according to number of atoms. Conversion from percentage by weight to atomic percentage with an alloy is mathematically the same as conversion from percentage by weight to percentage by volume with gaseous mixtures.

The above rule is simply the application to alloys of the laws of Raoult and Henry regarding the vapor pressure of solutions. Many measurements have shown that the vapor pressure of a chemical substance in a solution is proportional to its mol-fraction and that the lowering of the vapor pressure of a solution due to a nonvolatile component of fixed percentage is at all temperatures the same fraction of the vapor pressure of the pure solvent. Measurements of the vapor pressure of brass and other alloys, however, have shown that often Raoult's law does not hold. This is probably due to chemical combination among the constituents. Before discussing this point, an example will be given of calculation where the heat of combination can be neglected.

Example 44

Calculate the vapor pressure of half-and-half solder (50 per cent lead, 50 per cent tin) at 1200°C., neglecting any heat of combination. Calculate also the approximate normal boiling point of the solder.

Solution:

$$\begin{aligned} {}^{50}\!/\!_{207} &= 0.242 \text{ atom of Pb} \\ {}^{50}\!/\!_{119} &= \underline{0.420} \text{ atom of Sn} \\ & 0.662 \end{aligned}$$

$$\frac{0.242}{0.662} = 36.6 \text{ atomic per cent Pb.}$$

$$\frac{0.420}{0.662} = 63.4 \text{ atomic per cent Sn}$$

The maximum vapor pressure of Pb is given by the formula $\log p = -\frac{9{,}190}{T} + 7.445$. When $T = 1{,}473$, $p = 16.1$ mm.

The maximum vapor pressure of Sn is given by the formula $\log p = -\frac{14,800}{T} + 8.701$. When $T = 1,473$, $p = 0.045$ mm.

Partial vapor pressure of the Pb: $0.366 \times 16.1 = 5.89$ mm.
Partial vapor pressure of the Sn: $0.634 \times 0.045 = 0.03$
Vapor pressure of the solder: $= 5.92$ mm. (1)

Neglecting for a moment the vapor pressure of the tin, the vapor pressure of the alloy will be 760 mm. when that of the lead is $\frac{760}{0.366}$, or 2,075 mm. Substituting this for p in the vapor-pressure formula for Pb:

$$\log 2,075 = -\frac{9,190}{T} + 7.445,$$

whence

$$T = 2226°\text{K., or } t = 1953°\text{C. (first approximation).}$$

The vapor pressure of Sn at 1953°C is found to be 112.7 mm. $112.7 \times 0.634 = 71.5$ mm. excess from the Sn. Therefore, the Pb should support about 688.5 mm instead of 760.

$\frac{688.5}{0.366} = 1,881$ mm. Substituting this as above, $T = 2204°$K., or $t =$ approximately 1930°C. (2)

The foregoing calculation clearly illustrates why it is more and more difficult to remove an element from a mixture by distillation as the percentage of the element present grows smaller. The partial vapor pressure of the element grows smaller in direct proportion as the atomic percentage is reduced. In practice the temperature must be raised toward the end of a separation by distillation in order to counteract the effect of lowered partial vapor pressure. It is impossible to remove an element completely by distillation. In the Parkes process the zinc crusts commonly retain as much as 1 per cent zinc after distillation. There is also an important loss of mercury in retort bullion after distillation. In other cases it may be possible to reduce an element to a negligibly small percentage, if the element is sufficiently volatile.

Ultimate Composition of an Alloy Heated at Constant Temperature.—It is evident that, when an alloy or an impure metal is heated for a considerable time at a constant high temperature, at first its composition will change owing to greater vaporization of the elements with higher partial vapor pressures. As the atomic percentages of the more volatile elements become lower, the partial vapor pressures tend toward equality, and the alloy must approach a definite constant composition if the temperature remains unchanged (see Prob. 390).

Effect of Heat of Combination of the Elements in an Alloy.—In general the constituents of an alloy are not chemically free from each other but are united as a solution and sometimes as a chemical compound.

To break up this union, as must be done when one of the elements vaporizes from the alloy, requires energy equivalent to the heat of solution or the heat of formation of the compound. The total energy change in vaporization is then not simply the heat of vaporization but has an additional component.

The application of this principle in practice is uncertain. Data relating to the heat of combination of elements in alloys are almost altogether lacking, particularly for the liquid state. Though we may know, for example, the heat of formation of $CuAl_2$, presumably the same relation does not exist in the liquid alloy.

The heat of solution or of formation may be either positive or negative. If ΔH is positive, it represents additional energy available instead of energy required. This accounts for the fact that the vapor pressures of the elements in some alloys are greater than would be expected from their atomic percentages or mol-fractions in accordance with the rule stated above. A considerable number of data are available regarding the vapor pressures of mercury in amalgams. These show, as would be expected, that, in the case of amalgams having heats of formation with ΔH negative, the vapor pressure is less than that calculated from the mol-fraction and, in the case of amalgams having heats of formation with ΔH positive, the vapor pressure is greater than that calculated from the mol-fraction. This deviation from Raoult's law is explained by some writers on a purely chemical basis by assuming partial combination between the components (as $Cd + Hg = CdHg$), in the case of deviation below the normal, association of the atoms of one of the elements into molecules (as $2Zn = Zn_2$), in the case of deviation above the normal, and a special type of solution (the effect of which is satisfactorily expressed in an empirical formula by Van Laar) in cases not covered by either of the first two assumptions.[1] It seems probable that all these explanations are consistent with and directly related to the thermochemical viewpoint here suggested.

When experimental data are not available, it may be better in many cases to take account of the additional energy requirement in an approximate way rather than to neglect it altogether. For example, in calculating the vapor pressure of an amalgam, instead of using the vapor-pressure formula for pure mercury (in which $A = 3{,}066$ and $B = 7.752$), it would seem more accurate to use a modified formula in which A is redetermined by adding to Λ, in the expression $\Lambda = 4.58A$, the quantity of heat represented by the heat of formation of the amalgam, per mol of mercury. This is illustrated in the following example:

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[1] See papers by J. Hildebrand and associates, *Trans. Am. Electrochem. Soc.*, **22**, 319 (1913); *J. Am. Chem. Soc.*, **36**, 2020 (1914); **37**, 2452 (1915); **42**, 545 (1920).

Example 45

Calculate the vapor pressure of zinc at 700° and at 1000°C. in brass of ⅔ Cu, ⅓ Zn, (a) neglecting heat of combination between the zinc and copper, and (b) assuming a heat of combination of 20 cal. per gram of brass.

Solution:

$$\frac{66.7}{63.6} = 1.05 \text{ atoms Cu.} \qquad \frac{1.05}{1.56} = 67.3 \text{ atomic per cent Cu}$$

$$\frac{33.3}{65.4} = 0.51 \text{ atom Zn.} \qquad \frac{0.51}{1.56} = 32.7 \text{ atomic per cent Zn}$$

Vapor pressure of Zn: $\log p = -\frac{6{,}163}{T} + 8.108$

When $T = 973$, $p = 59$ mm

When $T = 1{,}273$, $p = 1{,}840$ mm.

$0.327 \times 59 = 19$ mm. for Zn in brass at 700°C.

$0.327 \times 1{,}840 = 600$ mm. for Zn in brass at 1000°C. (1)

$20 \times 3 = 60$ cal per gram of Zn $60 \times 65.4 = 3{,}920$ cal per mol of Zn, to be supplied in addition to the heat of vaporization. The new value of $A = 6{,}163 + \frac{3{,}920}{4.58} = 7{,}020$.

The new value of B must be determined, as in previous illustrations, from a pair of values for p and T to be substituted in the equation

$$\log p = -\frac{7{,}020}{T} + B.$$

In general no such pair of values will be known. In the case of brass, some figures are available, shown in Table VII. According to these, the partial vapor pressure of the zinc in the brass containing 32.7 atomic per cent zinc should be 0.18 times that of pure zinc, in the temperature range 900 to 1350°C. At 1000°C., the vapor pressure of pure zinc is 1,840 mm. $0.18 \times 1{,}840 = 332$ mm.

Substituting above the pair of values $t = 1{,}000$, $p = 332$, $\log 332 = -\frac{7{,}020}{1{,}273} + B$, whence $B = 8.04$

Now using the new values of A and B:

When $T = 973$, $p = 6.7$ mm.[1]

$T = 1{,}273$, $p = 332.0$ mm. (2).

It will be noted that the values obtained in (2) are considerably lower than those in (1). That this should be the case is borne out by actual measurements of the partial vapor pressures of zinc in brass. Table VII* gives the results derived by J. Johnston from the measurements of Lohr, Hansen, and others.

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[1] This result is substantiated by the subsequent experimental determination of R. Hargreaves, *J. Inst. Metals*, **64**, 115 (1939).

* "International Critical Tables," Vol. III, p. 284, McGraw-Hill Book Company, Inc., New York, 1928.

TABLE VII.—PARTIAL VAPOR PRESSURES OF ZINC IN BRASS
(Temperature range 900–1350°C.)

Atomic per cent, zinc in brass	Partial pressure of zinc in per cent of pressure of pure zinc	Atomic per cent, zinc in brass	Partial pressure of zinc in per cent of pressure of pure zinc
10	2	30	15
15	3	35	21
20	6	40	27
25	10	45	32

Because of the method used to determine the value of B in the revised formula, $\log p = -\frac{7{,}020}{T} + 8.04$, the value obtained for p at 1000°C. must coincide with that indicated in the above table. At other temperatures, exact agreement is not to be expected, owing in part to the fact that the method is an approximation and in part to the fact that the figure used in the calculation of the new value of A, though an experimentally determined one, may be far from accurate. To test the agreement at other temperatures, let us determine the partial pressure of zinc in this brass at 1300°C.:

By the formula:

$$\log p = -\frac{7{,}020}{1{,}573} + 8.04 \qquad p = 3{,}700 \text{ mm.}$$

By the table:

$$p = 0.18 \times p \text{ for pure zinc at 1300°C.} = 0.18 \times 15{,}500 = 2{,}800 \text{ mm.}$$

In view of the rapid change in the vapor pressure between these temperatures, the difference is not great. The formula in this case is probably a less accurate means of estimating the partial vapor pressure than the tabulated data, but the principle illustrated is applicable when no tabulated data are available.

When a definite chemical compound is formed, the principle just applied may usually be inapplicable. For example, one cannot study the vapor pressure of NaCl from the vapor pressures of Na and Cl. Many intermetallic compounds, however, are chemically so weak—the free energy of combination is so small—that the principle may be used as an approximation.

An element may sometimes exist in an alloy partly as a definite chemical compound and partly as uncombined (but dissolved) substance in excess of that in the compound. In this case the mol-fraction determining the vapor pressure of the element would be, not that corresponding to the total amount of the element present, but only that corresponding to the uncombined part. In addition, there would be the vapor pressure of the compound, which in some cases might be a relatively large amount.

Summary.—The following statements summarize the principal facts with regard to calculation of the vapor pressure of alloys:

1. It is not possible to make precise calculations of the vapor pressure of alloys, owing to disturbing factors.
2. In many cases, however, it is possible to make calculations sufficiently accurate to be useful.
3. The vapor pressure of an element contained in solution in an alloy is always less than that of the pure element.
4. In the absence of disturbing factors, the vapor pressure of an element in an alloy would be equal to the vapor pressure of the pure element multiplied by the mol-fraction present in the alloy.
5. One of the principal disturbing factors is heat of combination between the constituents of an alloy, which tends to hold the element in the alloy and accordingly reduces its vapor pressure below the amount called for in item 4. When the heat of combination is known, this factor may be partly allowed for by recomputing the constants A and B in the $\log p$ formula, adding the heat of combination to the heat of vaporization in determining the value of A.

The Surface as a Factor in Vapor Pressure.—Consider the vaporization of solid brass. As soon as some zinc has vaporized, since the vaporization takes place mainly from the surface the composition of the surface is altered. The vapor pressure then becomes more nearly that of an alloy lower in zinc. Evidently the vapor pressure of an alloy in the solid state becomes a very uncertain factor and not subject to precise calculation.

The same factor has some influence on the vapor pressure of a liquid alloy, *viz.*, the rate of diffusion of the more volatile element from the interior to the surface has an effect on the vapor pressure. If the melt is being stirred, this factor is probably negligible.

The vapor pressure of a pure metal also is affected by its surface if the surface is oxidized or otherwise altered. For this reason the vapor pressure of a metal may vary with the nature of the atmosphere above it. The vapor pressure of solid brass has been found to be considerably lower in an atmosphere of air than in an atmosphere of hydrogen. A metal bath also will not exhibit its normal vapor pressure when covered with a layer of slag.

The effect of the furnace atmosphere on vapor pressure has been investigated in connection with molten brass by C. Upthegrove and A. J. Herzig at the University of Michigan.[1] The results of their experiments bring out strikingly the effect of an oxide crust in reducing volatilization of zinc. The crust was effective, however, only up to the boiling point of the brass. It was found that with high-zinc brasses the volatilization loss exceeded the oxidation loss, and it was concluded that such brasses should be melted in oxidizing atmospheres, while low-zinc alloys should be melted in neutral atmospheres.

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[1] "The Effect of the Products of Combustion on the Shrinkage of Metal in the Brass Industry," *Eng. Research Bull.* 22, December, 1931.

APPLICATION TO REACTION PRESSURES

The thermodynamic relations involved in the reversible process of chemical decomposition of a compound with formation of a gas are similar to those involved in the process of vaporization. The heat absorbed in the decomposition (per mol of gas formed) is analogous to the heat absorbed in vaporization. The pressure of the gas formed, called the "reaction pressure," is analogous to the vapor pressure. It may be expressed as a function of the absolute temperature. An equation of the simple form $\log p = -\frac{A}{T} + B$ may be deduced which will give approximately the relation between p and T, A being determined from the heat of the reaction and B from any known pair of values for p and T. $A = \frac{-\Delta H_0}{4.58}$, where ΔH_0 is the heat of the reaction at 0°K. in calories per mol of gas formed.[1] While the equation of this form does not represent the actual curve precisely, the accuracy is sufficient for practical purposes. The exact equation, derived from free-energy data, is of more inconvenient form and contains constants which in many cases cannot be accurately determined in view of the present absence of data.

If it is known that the vapor pressure of a liquid at a certain temperature is, say 5 mm., it follows that the action of vaporization will be reversed (to condensation) when the partial pressure of the vapor already formed exceeds 5 mm. Likewise, if it is known that the reaction pressure of a certain reversible gas-forming reaction is 5 mm., it follows that the reaction will be reversed if the partial pressure of the gas already present exceeds 5 mm., temperature remaining constant.

Before an example is given, it may be well to note that gas pressures in many chemical reactions may be calculated from the equilibrium constant K.

Consider now the metallurgically important reaction

$CaCO_3 = CaO + CO_2$; $\Delta H = +40{,}600$ cal. (at 18°C.), when the carbon is taken as amorphous

$$A = \frac{40{,}600}{4.58} = 8{,}865.$$

$$\log p = -\frac{8{,}865}{T} + B.$$

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[1] At 0°K. the heat of reaction and the free-energy change are identical.

In this, substitute the experimentally determined pair of values, $p = 760$, when $t = 882°C$. (Andrussow).

$$2.881 = -\frac{8,865}{1,155} + B. \qquad B = 10.556.$$

The following table compares the value of the reaction pressure as calculated from these values of A and B with the values experimentally determined by L. Andrussow.[1]

TABLE VIII.—COMPARISON OF CALCULATED AND OBSERVED REACTION PRESSURES, $CaCO_3 = CaO + CO_2$

Temperature, °C	Pressure, millimeters		Temperature, °C	Pressure, millimeters	
	Observed	Calculated		Observed	Calculated
20	*2.2×10^{-20}	2.0×10^{-20}	700	31.4	27.9
200	*7.8×10^{-9}	6.5×10^{-9}	800	208	197
500	0.15	0.12	900	992	995
600	3.3	2.5	1000	*3,580	3,910

* Calculated by Andrussow by extrapolation from observed data.

As in the case of vapor-pressure equations, the equation may be expressed more accurately in a more elaborate form, such as:

$$\log p = \frac{-\Delta H_0}{4.578T} - aT + 1.75 \log T + b,$$

in which the constants a and b can be determined from measurements of reaction pressures after the manner given below. Strictly it is not correct to base calculations involving equilibrium, as above, on heats of reaction alone, since equilibrium is determined by free-energy change (see Chap. XXIV).

When the log p equation is to be applied at temperatures above the melting point or the boiling point of one of the substances involved in the reaction, the additional energy change of fusion or vaporization must be taken into account. This is best done by calculating the heat of the reaction at elevated temperature, near the temperature at which the reaction will take place. For example, the heat of the reaction $ZnO + C = Zn + CO$ is $\Delta H_{18} = 54,340$ cal. at 18° and is $\Delta H_{857} = 84,250$ cal. at 857°, the Zn being liberated as vapor in the latter case. Accordingly the latter value is used, as on page 364, whenever the zinc is in the vapor state.

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[1] *Z. physik. Chem.*, **116**, 81 (1925).

As a further example, consider the roast reaction in lead smelting:

$$2PbO + PbS = 3Pb + SO_2; \qquad \Delta H = +56{,}260 \text{ cal. (at } 18°).$$

At the furnace temperatures, the lead is produced in the liquid state. Let us calculate the heat of this reaction at 800°C. The mean specific heats of the PbO and PbS are not definitely known at this temperature but can be estimated from the data given in Table XIX, page 397.

Heat content above 18° of:

$$\begin{aligned} 2PbO \text{ at } 800° &= 2 \times 223 \times 0.0560 \times 782 &&= 19{,}550 \text{ cal.} \\ PbS &= 239 \times 0.0559 \times 782 &&= 10{,}450 \\ 3Pb &= 3 \times 207 \times [16.4 + 0.033(800 - 327)] &&= 19{,}870 \\ SO_2 &= 22.4(0.406 + 0.00009 \times 818)782 &&= 8{,}400 \end{aligned}$$

The heat of the reaction at 800° then is $\Delta H = +56{,}260 - 19{,}550 - 10{,}450 + 19{,}870 + 8{,}400 = +54{,}530$ cal. Then, $A = \frac{54{,}530}{4.58} = 11{,}900$.

Using the observed values $p = 99$ mm when $t = 800°C.$, we have $\log 99 = -\frac{11{,}900}{1{,}073} + B$. $B = 13.09$.

The following table compares the reaction pressures as calculated from these constants, with the values observed by Schenck and Rassbach, and gives also the calculated reaction pressure at 500°C., which is below the measurable range, and the calculated normal reaction temperature.

TABLE IX.—CALCULATED AND OBSERVED REACTION PRESSURES,[1] $2PbO + PbS = 3Pb + SO_2$

Temperature, degrees Centigrade	Pressure, millimeters		Temperature, degrees Centigrade	Pressure, millimeters	
	Observed	Calculated		Observed	Calculated
500		0 0050	776	60	56
692	6	5 8	824	276	174
751	39	30	893		760

[1] Observed values by Schenck and Rassbach, 1907

Determination of the Constants A and B from Measurements of Reaction Pressures.—Instead of using the heat of the reaction for derivation of the constant A and then a known pair of values of p and T for derivation of B, one may determine A and B from any two pairs of values of p and T through solution of two simultaneous equations. This method has already been given on page 350 for determination of A and B in the vapor-pressure expression.

As an example, consider again the decomposition of $CaCO_3$. In addition to the values $p = 760$, when $t = 882°C.$, Andrussow also found $p = 3.3$ mm., when $t = 600°C.$ These values give the equations

$$\log 760 = -\frac{A}{1{,}155} + B$$

and

$$\log 3.3 = -\frac{A}{873} + B.$$

Solving, we find $A = 8{,}767$. $B = 10.56$.

These values are close to those determined from the heat of the reaction at 18° (page 361).

Since $\Delta H = -4.58A$, the heat of a reaction may also be estimated from reaction-pressure data, A being calculated from two pairs of values of p and T.

For example, from data shown in Table IX for the reaction $2PbO + PbS = 3Pb + SO_2$, the following equations are derived:

$$\log 6 = -\frac{A}{965} + B$$

and

$$\log 276 = -\frac{A}{1{,}097} + B$$

Solving simultaneously, we find $A = -13{,}340$. $B = 14\ 60$

Then $\Delta H = -4.58A = -4\ 58 \times (-13{,}340) = 61{,}100$ cal This value compares with the figure 54,530 cal., obtained on page 362.

This method of estimating a heat of reaction is of course limited to certain types of reactions; even where applicable, it is not to be recommended in comparison with other methods of greater accuracy.

Calculation of Temperatures of Continuous Reduction of Zinc Oxide by Carbon.—Zinc reduction is discussed at the beginning of Chap. XXII. C. G. Maier[1] has made a precise calculation of the temperatures of continuous reduction of zinc oxide by carbon at different pressures. It will be of interest to calculate these temperatures by the approximation method just described and compare the results with the accurate calculations of Maier.

The reaction at 18°C. is:

$$ZnO + C = Zn + CO; \qquad \Delta H = +54{,}340 \text{ cal.}$$

Derivation of the constants A and B requires the heat of the reaction at the elevated temperature where Zn is liberated as vapor. This may best be the temperature for continuous reduction at 760 mm., and Maier's figure of 857°C. will be adopted. The heat content gained by ZnO, C, Zn, and CO between 18 and 857° must be calculated first. The results are 8,620, 3,430, 35,800, and 6,160 cal., respectively. The heat of the reaction at 857° is therefore $\Delta H = 54{,}340 - 8{,}620 - 3{,}430 + 35{,}800 + 6{,}160 = +84{,}250$ cal. (Actually these values are the heat contents above 0° instead of 18°; since two are on each side of the equation, the difference is very slight. In computing the heat content of Zn at 857°, account was taken of the fact that the zinc vaporizes at 847°, not at its normal boiling point. See page 334).

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[1] *Op. cit.*

Since the reaction forms 2 mols of gas, $A = \frac{84{,}250}{2 \times 4.58} = 9{,}200$.

Then, $\log 760 = -\frac{9{,}200}{857 + 273} + B$. $B = 11.02$.

The relation is therefore:

$$\log p = -\frac{9{,}200}{T} + 11.02.$$

The comparative results are as follows[1]:

TABLE X.—TEMPERATURES OF CONTINUOUS REDUCTION OF ZINC OXIDE BY CARBON

Pressure, millimeters	Temperature, degrees Centigrade	
	Precise values (Maier)	Calculated by above formula
7.6	637.5	634
76	733	733
760	857	857
7,600	1,014	1,015
76,000	1,230	1,225
760,000	1,534	1,516

Though the agreement is excellent, it should be noted that the approximate method used here requires one pair of values (usually made available by experimental data) as a starting point. If the starting-point values are inaccurate, the results from the derived equation will also be inaccurate. The method used by Maier does not require direct determination of a pair of values but obtains all values from the equilibrium constants at various temperatures and pressures of the reactions $ZnO + CO = Zn + CO_2$ and $CO_2 + C = 2CO$. A method of that kind should be used whenever possible; unfortunately few of the necessary data are available at the present time. Space cannot be given here for details of the method used by Maier; it is covered excellently in a bulletin[1] which contains also much other valuable material.

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[1] In Maier's calculations the heat of formation of CO at 18°C. has been taken as 26,320 cal., the value for pure crystalline carbon (as graphite). The author has used 29,160 cal., an average value for amorphous carbon, which would seem more in agreement with the conditions of practice. The uncertainty regarding the heats of oxidation of carbon is unfortunate, but in the present instance the difference in the final results is small. Use of the value 26,320 instead of 29,160 would alter the figure 634 in Table X to 640 and the figure 1,516 to 1,483.

Problems

379. 1. The normal boiling point of copper is 2600°C. Calculate the latent heat of vaporization of 1 kg. of copper from Trouton's rule. What is the percentage difference between this calculated value and the value given in the tables?

2. Using the value for Λ as determined by Trouton's rule and the thermodynamic relation $\Lambda = 4.58A$, determine the constants A and B in the formula $\log p = -\frac{A}{T} + B$ for the vapor tension of molten copper Compare results with the values given in the tables.

3. Calculate the vapor tension of copper at its melting point, using formula derived in 2.

4. From the formula derived in 2 and the vapor tension obtained in 3, derive the constants A' and B' in the formula $\log p = -\frac{A'}{T} + B'$ for the vapor tension of solid copper (see tables for the heat of fusion).

380. 1. Calculate the normal boiling point of silver from its latent heat of vaporization, using Trouton's rule

2. Using the latent heat of vaporization, calculate the constants A and B in the formula $\log p = -\frac{A}{T} + B$ for the vapor tension of molten silver

3. Calculate the constants A' and B' for the vapor tension of solid silver.

4. What is the vapor tension of silver at 27°C and at 2500°C ? (Use constants given in tables.)

5. A silver melting furnace burns 40 kg of oil (C, 85 per cent; H, 15) per hour, using 50 per cent excess air. The furnace contains molten silver 3 hr. per day 300 days per year What is the annual loss of silver through vaporization if the average temperature of the surface of the bath is (*a*) 1050°C , (*b*) 1150°C., assuming the gases in both cases to become 25 per cent saturated with silver vapor?

381. 1. Given that the normal boiling point of lead is 1740°C , calculate the latent heat of vaporization of 1 kg of lead from Trouton's rule Compare with value given in the tables.

2. Using the calculated values and the thermodynamic relation $\Lambda = 4.58A$, calculate the constants A and B in the formula $\log p = -\frac{A}{T} + B$ for the vapor tension of liquid lead.

3. From the constants derived, calculate the vapor tension of lead at its melting point.

4. Using this vapor tension and given the latent heat of fusion of 1 kg. of lead = 5.9 Cal., evaluate the constants A' and B' for the vapor tension of solid lead from the calculated formula for liquid lead.

5. What are the vapor tensions of the lead and the zinc in a dezincing furnace at the start of the operation, with the furnace temperature at 1000°C.? Assume that the alloy is 99.4 per cent Pb and 0.6 per cent Zn by weight. Use constants given in tables.

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[1] *U. S. Bur. Mines, Bull.* 324, 1930.

382. Given the following constants for zinc:
Atomic weight, 65.4
Melting point, 419°C.
Normal boiling point, 905°C.
Latent heat of fusion, 24.4 Cal. per kg.
In the vapor-tension formula for liquid zinc, $A = 6{,}163$, $B = 8.108$.

Required: 1. The latent heat of vaporization, per kilogram, calculated by two methods, and the percentage by which each differs from Maier's value of 426 Cal. per kilogram.

2. The vapor-tension formula for solid zinc, as derived from the constants given above for liquid zinc.

3. The vapor pressure of zinc at the melting point of tin (232°C.) and at the melting point of copper (1084°C.).

4 Assuming a mixture of 55 per cent CO and 45 per cent Zn vapor at 1084°C in a retort open to the atmosphere at the barometric pressure of 725 mm, what would be the partial pressure of the zinc vapor? What percentage of the zinc vapor would condense if the temperature were lowered to 750°C.?

383. In the electrothermic method of producing magnesium, the metal is reduced as vapor and condensed. It is then redistilled at lower temperature in order to obtain it in coalesced liquid form of high purity. This may be done at 1000°C at reduced pressure or by sublimation at about 600°C in a partial vacuum.

The vapor pressure of magnesium is stated to be 7.6 mm at 727°C and 370 mm. at 1027°C.

Required: 1. The constants A and B in the log p formula for the vapor pressure of magnesium, as derived from the above pressures.

2. The normal boiling point of magnesium, calculated from these derived constants.

3. The pressure at which the boiling point is 1000°C

4. From the latent heat of fusion and the vapor pressure at the melting point, determine the constants A and B in the log p formula for solid magnesium

5. The required vacuum for active sublimation at 600°C., in millimeters of mercury.

384. 1. The normal boiling point of zinc is 905°C Calculate the latent heat of vaporization of 1 kg. of zinc from Trouton's rule

2. Using the thermodynamic relation $\Lambda = 4.58A$, determine the constants A and B in the formula $\log p = -\frac{A}{T} + B$ for the vapor tension of molten zinc

3. Calculate the vapor tension of zinc at its melting point, using formula derived in 2.

4. From the formula derived in 2 and the vapor tension obtained in 3, derive the constants A' and B' in the formula $\log p = -\frac{A'}{T} + B'$ for the vapor tension of solid zinc.

5. Calculate the vapor tension of zinc at 20°C. and at 3000°C., using constants given in tables.

6. Calculate the vapor tension of Zamak-3 (the New Jersey Zinc Company's die-casting alloy), containing 96 per cent Zn, 4 Al, at 905°C

7. Calculate the approximate normal boiling point of Zamak-3.

385. 1. Determine the constants A and B in the formula $\log p = -\frac{A}{T} + B$ for the vapor tension of molten silver, using the latent heat of vaporization as given in the tables.

2. What is the vapor tension of silver at 800°C. and at 3000°C.? (Use constants given in tables.)

3. What is the vapor tension of an alloy of 3 parts silver to 1 part gold by weight at 1210°C.?

4. How many grams of silver and of gold would be carried out daily in the gases of a furnace melting the alloy above, in which the gases become one-third saturated with both metals at a temperature of 1210°C., the volume of the gases being 680 cu. m. per day?

5. Is the vapor tension of silver equal to that of gold at any temperature? If so, at what temperature?

386. The following values are points on the vapor-tension curve for mercury:

Pressure 760 mm., temperature 357°C.
Pressure 100 mm., temperature 261°C.
Pressure 1.8 mm., temperature 140°C.

Required. 1. Derive a formula for the vapor tension in terms of T of the form $\log p = -\frac{A}{T} + 1.75 \log T - ET + C$ (Nernst).

2. Evaluate this for the vapor tension of mercury at its freezing point (−39°C.) and at 0, 100, and 500°C.

3. If λ (the molal latent heat of vaporization) = $4.578(A + 0.767T - ET^2)$, calculate λ for T = 630, 373, 273, and 234°K. (melting point)

4. Calculate the weight (in milligrams) of mercury vapor carried out of a condenser by each (standard) cubic meter of inert gas, at 373°K. and at 273°K., using pressures calculated in requirement 2.

387. The zinc crust distilled in a Faber-du-Faur furnace has the following composition:

	Per Cent
Zn	50.0
Pb	36.5
Ag	13.0
Cd	0.5

It is charged in the retort, and distillation is commenced at 980°C. At the end of the process the temperature has been raised to 1200°, and the composition of the remaining alloy is then as follows:

	Per Cent
Zn	0.5
Cd	0.003
Pb, Ag	Balance

Required. 1. The vapor tension of the alloy at the start of the process; and the percentage composition of the vapor coming off, by weight.

2. The same, at the end of the process.

388. A sample of white gold contains 14 per cent Ni, 6 Zn, 80 Au.

Sterling silver contains 92.5 per cent Ag, 7.5 per cent Cu.

Neglect any heat of combination between the constituents.

Required: 1. The vapor tension of pure silver and of sterling silver, at 1200°C.

2. The vapor tension of pure gold and of the above white gold, at 1200°C.

3. The normal boiling point of (*a*) the white gold and (*b*) sterling silver.

389. 900 g. of platinum and 100 g. of rhodium are melted in a crucible in a small induction furnace for the purpose of making thermocouple wire. Platinum has a melting point of 1755°C. and a boiling point of 4300°C. Rhodium has a melting point of 1985°C. and a boiling point of 2500°C.

The crucible was left uncovered, and a draft of air passed over the surface of the melt. Assume that 2 cu. m. of air (measured at standard conditions) thus came in contact with the surface, attaining practically the temperature of the metal, and becoming 5 per cent saturated with the metallic vapor coming off. The average temperature of the surface of the melt is 2050°C.

Required: 1. The vapor tension of the melted alloy, at 2050°.

2. The grams of platinum and of rhodium lost by volatilization.

3. If the crucible, containing, besides the metal, dry air at 20°C., 760 mm. at the start of the heating, had then been closed and made gastight, what total pressure would have resulted in it at 2050°, and what would then have been the percentage composition (by volume) of the gases in the crucible?

390. The zinc crust from a Parkes desilverizing kettle, containing 11 per cent silver, 65 lead, 24 zinc, is distilled in a Faber-du-Faur retort furnace, which reduces the zinc content to 0.5 per cent. The temperature in the retort at the start is 950°C., at the end 1200°C.

Required: 1. The percentage composition by weight of the vapor coming off at the start of the distillation.

2. The same, at the end of the operation

3. The ratio of the total volume of vapor coming off per second at the end to that at the beginning of the process.

4. The same, by weight.

5. The ultimate composition (by weight) of the molten alloy (and of the distillate) if kept an indefinitely long time at 1200°C

391. Prime Western zinc is refined by redistillation. The zinc placed in the retorts analyzes as follows:

	Per Cent
Pb	1.4
Cd	1.0
Zn	Remainder

The iron content of the zinc is neglected because of the small percentage and low vapor pressure. Some carbon is charged, and it may be assumed that no oxidation occurs in the retort or in the condenser

The temperature in the retort is held at 950°C. The vapors enter the condenser at 950° and leave at 500°C

Required: 1. The total vapor pressure of the metal in the retort at 950° if the retort were sealed.

2. With the retort not sealed, what are the percentages of cadmium and of lead by weight in the metallic vapor coming from the retort at the start of the process?

3. What proportion of each metal (zinc, lead, and cadmium) entering the condenser escapes as uncondensed vapor?

392. The ore charged into a zinc retort had the following composition.

	Per Cent
Zn	70.0
CdO	0.8
PbO	1.0
S(as ZnS)	1.2
SiO_2, etc.	10.0

This is mixed with 40 per cent of its weight of anthracite coal, containing 85 per cent C and 15 per cent SiO_2. The retort holds 100 lb. of this mixture. The gases leave the retort at 1250°, the condenser at 600°, and the prolong at 400°C. Assume all Zn volatilized except that combined with S. Assume Cd and Pb volatilized uniformly with the Zn over a period of 20 hr.

Required: 1. What percentage of the Cd and Pb in the charge will be carried out with the Zn?

2. What percentages of the Zn, Cd, and Pb entering the condensers are recovered in the condensers and in the prolongs, and what percentages are lost uncondensed?

3. The average percentage composition of the contents of the condenser and the prolong, neglecting oxidation to blue powder.

393. A zinc scum from the Parkes process contains Zn, 60 per cent, Pb, 35; Ag, 5. It is distilled in a Faber-du-Faur furnace, the vapors coming off at 760 mm. pressure. Assume:

$$(Pb, Zn_6) = 5{,}000 \text{ (not known)}.$$
$$(Pb_{19}, Zn) = 23{,}188 \text{ (determined)}.$$

Neglect the heat of combination of Pb and Zn with Ag.

Required: 1. Calculate the molecular (atomic) percentage of each metal in the alloy.

2. At what temperature will the metallic vapors first come off under 760 mm pressure?

3. What will be the composition of this distillate?

4. At what temperature will the residue in the retort contain 19 Pb:1 Zn?

5 What will be the composition of the distillate at this temperature?

394. The boiling point of phosphorus is 280°C. It should therefore be possible to dephosphorize pig iron to a very low percentage of phosphorus by simple heating, provided there be no heat of combination between phosphorus and other elements in the pig iron.

According to Richards, the heat of combination of phosphorus with Fe is negligible He gives $(Fe, P) = 0$ cal. But $(Mn_3, P_2) = 70{,}900$ cal., or 1,144 Cal. per kilogram of P Although the Mn forms other compounds with P as well as with Fe, for which no heats of formation are known, the above figure may be used as a basis of calculation. C and Si probably have no effect on the phosphorus

Given the composition of a basic pig iron:

	Per Cent
Fe	93.0
C	3.8
Si	0.9
Mn	1.7
P	0.6

Required: 1. The vapor tension of each constituent at 1700°C., each considered alone as the pure element. (Use more accurate form of formula for phosphorus.)

2. The vapor tension of the pig iron at 1700°C., if it be considered as a solution of the elements given without heats of combination.

3. The formula for the vapor tension of phosphorus combined as Mn_3P_2, as modified by the heat of formation of that compound.

4. The normal boiling point of phosphorus from Mn_3P_2, as calculated from the modified formula.

5. The vapor tension of the phosphorus in the pig iron at 1700°, as calculated from the modified formula and the amount present.

6. With this vapor tension, what percentage of the phosphorus present in a 20-ton charge of the above pig iron would be volatilized from an acid Bessemer converter at 1700°C., with 6,500 cu. m. of gas issuing from the mouth of the converter during the blow, neglecting the decrease in vapor tension as the phosphorus is removed? (Here assume that the gases become 1 per cent saturated with phosphorus vapor, which corresponds approximately with the atomic percentage of phosphorus in the pig iron.)

395. At a Western gold mill the squeezed amalgam charged into the retorts contained:

	Per Cent
Au	32
Ag	8
Hg	60

The temperature in the retort was raised quickly to 400°C. and then slowly to 800°, at which it was held until the remaining bullion reached the composition for which 800° is the boiling point.

Required: 1. The vapor tension of the amalgam at 400°C., disregarding the heats of combination of its constituents.

2. The normal boiling point of the amalgam as charged.

3. The percentage composition of the bullion left at the end of the process

4. What temperature must be reached in order to eliminate all but 0.5 per cent Hg?

5. From the latent heat of vaporization of mercury and the relation $\Lambda = 4.58A$, determine the constants A and B in the formula $\log p = -\frac{A}{T} + B$ for the vapor tension of liquid mercury.

6. Determine the value of the constant A when the above formula is modified by the heats of combination of Hg with Au and Ag in the amalgam.

7. Using the above value of A and assuming B to remain unchanged, calculate the vapor tension of the amalgam at 400°C.

8. According to this formula, what temperature would need to be reached in order to eliminate all but 0.5 per cent Hg in the bullion?

Heat of formation of gold amalgam, 13 Cal. per kilogram of Au; of silver amalgam, 23 Cal. per kilogram of Ag

NOTE: Since the temperatures of requirements 1 to 7 are below the melting points of Au and Ag, the vapor tensions of these elements are so small that they may be neglected.

396. *a.* The reaction pressure for the reaction $ZnS + 3CaSO_4 = 3CaO + ZnO + 4SO_2$ was determined by Trautz and Pakschwer to be 156 mm. at 1020°C.

Required: 1. The constants A and B in an equation of the form $\log p = -\frac{A}{T} + B$, giving the reaction pressures for this reaction.

2. Determine the reaction pressure at 900°C.; also, determine the temperature at which the reaction pressure will be 760 mm.

b. For the reaction $CuO.CuSO_4 + Cu_2O = 4CuO + SO_2$ the reaction pressure at 644°C. is 39.5 mm.; at 754°C., 419 mm. (Kelley).

Required: 1. The constants A and B in the $\log p$ equation for this reaction.

2. The temperature at which the reaction pressure is 760 mm.

3. The approximate heat of the reaction, as determined from the value of the constant A. Compare with the value for the heat of the reaction determined from the heats of formation given in the tables, disregarding the heat of combination of CuO with $CuSO_4$.

397. Magnesium is produced in the electrothermic process according to the reaction

$$\mathrm{MgO + C = Mg + CO.}$$

The reaction proceeds under normal atmospheric pressure at approximately 1800°C. but does not become sufficiently rapid below 2000°C.

Required: 1. The heat of the reaction at 1800°C

2. The constants A and B in an equation of the form $\log p = -\frac{A}{T} + B$ for the reaction pressure.

3. The reaction pressure at 2000°C.

4. In a reduction unit having a power consumption of 12.3 kw.-hr per pound of magnesium, what is the thermal efficiency, assuming the magnesium produced as vapor at 1800°C ?

398. 1. Assuming that, under standard pressure, the reduction of CdO by C begins at 580°C. and the heat absorbed in the reduction at this temperature is 37,200 cal. per mol, derive a formula of the form $\log p = -\frac{A}{T} + B$ which will show the relation between the temperature and the reaction pressure.

2. From this formula calculate the temperatures at which reduction will take place under pressures of 0.1 atm and 10 atm

3. Prove numerically that the cadmium obtained will be in the liquid state when the pressure in the retort is 1 atm

4. Working at a pressure of 0.1 atm , would any cadmium remain as liquid in the retort?

5. At what reduction temperature and pressure in the retort would the cadmium begin to be reduced as vapor?

399. The reduction of roasted Joplin concentrates according to the reaction

$$\mathrm{ZnO + C = Zn + CO}$$

was believed to begin at 940°C. (Ingalls) under normal pressure of 760 mm.

The reduction is carried out in retorts having the shape of hollow cylinders 4 ft (120 cm.) long, 8 in. (20 cm.) in diameter, inside dimensions These are made of fire clay having a resistivity of 60 thermal ohms at 1350°C. The outside temperature of the retorts averages 1400°C. when the working temperature inside is 1300°C.

Required: 1. The heat of the reaction at 940°, *i e* , the heat which must be supplied per 65.38 kg. of zinc to allow the reaction to proceed at this temperature.

2. The numerical values of A and B in the log p formula, taking this value of the heat of the reaction for ΔH.

3. The temperatures at which reduction would proceed under 0.2 atm. pressure and under 5 atm. pressure

4. The reaction pressure at 1300°C. (average retort temperature during distillation in practice).

5. If working at 5 atm. pressure in the retorts, would any zinc condense to liquid in the retort? Explain your answer.

6. At what temperature in the condenser will zinc begin to condense if the pressure is atmospheric?

7. At what temperature will it be 99 per cent condensed?

8. If the retort is closed and the temperature gradually raised, will it be possible for liquid zinc to form in the retort? If so, at what temperature and pressure?

9. If the gases leave the condenser at 500°C., what percentage of the zinc escapes in them uncondensed?

10. How much heat must be supplied to the charge per kilogram of zinc in order to keep the reduction proceeding at 1300°C.?

11. How much heat enters the retort through the walls per hour if the walls are (*a*) 5 cm. thick, (*b*) 2½ cm. thick?

12. How many kilograms of zinc can be reduced per hour, in each of the above cases?

13. What temperature should be maintained on the outside of the retorts in order to reduce 2 kg. of zinc per hour at the working temperature of 1300°C. inside the retorts?

400. Following are values of the pressure of CO_2 in the reaction $CaCO_3 = CaO + CO_2$ as determined by Smyth and Adams (1923):

(1)	550°C.	0.41 mm.
(2)	700°C	22.2 mm.
(3)	897°C.	760 mm.
(4)	1000°C.	2,942 mm.

Required: 1. From observations 1 and 4, determine the values of A and B in an equation of the form $\log p = -\frac{A}{T} + B$.

2. Calculate the heat of the reaction at 0°K. ($-\Delta H_0 = 4.58A$.) Compare with the thermochemical value of the heat of the reaction at 18°C.

3. From observations 1, 2, and 4, deduce a formula of the type $\log p = -\frac{A}{T} + 1.75 \log T - cT + d$. From this formula and also from the formula derived in requirement 1, compute the value of p at 1200°C.

4. Calculate ΔH_T, the heat of the reaction at $T°$, from the relation $-\Delta H_T = 4.58 (A + 0.743T - cT^2)$, for the temperatures 18° and 900°C. Compare with the thermochemical values at these temperatures.

CHAPTER XXIV

THERMODYNAMICS OF CHEMICAL REACTIONS

The energy changes associated with chemical reactions are a most important consideration in metallurgy, particularly in furnace processes and in electrolysis. We have for the most part in this book been concerned with the total energy change, or "heat of reaction," denoted by ΔH, which is most useful to the metallurgist in calculating the heat requirements and the heat balance of a furnace or process. However, in Chap. XVI, Electrolytic Processes, it has been pointed out that the reaction potential of an electrolytic cell depends directly, not on ΔH, but on the free energy of the reaction in the cell, denoted by ΔF. Likewise, in Chap. XXIII, Vapor Pressure and Temperature-Pressure Reactions, it has been stated that the derivation of a precise equation for the temperature-pressure relation must be based on the free-energy change. In both these cases we have as a matter of practical simplification used ΔH instead of ΔF in certain calculations. The taking of this liberty may in the calculation of cell potentials result in a large error; in the log p equation for vapor pressure or reaction pressure it is of less consequence because deviation in the value of A is largely compensated for, over a practical temperature range, by the form of the equation and proper adjustment of the value of B in the evaluation of these constants.

It is our purpose in the present chapter to discuss the relation between ΔH and ΔF, to show the derivation of the free-energy equation and how ΔF may be obtained, and to point out certain types of problems for which a knowledge of ΔF is essential. Unfortunately neither the relations nor the operations involved are simple; a full exposition of them would require theoretical discussion beyond the scope of this book and would need more space than can be given. For this reason no problems will be appended to this chapter, but it is hoped that the material given will form a useful extension of what has gone before and an introduction to a subject which may profitably be pursued further. To the latter end a brief bibliography will be given.

HEAT OF REACTION AND FREE-ENERGY CHANGE

The energy changes accompanying a chemical reaction are expressed in the well-known equation

$$\Delta H = \Delta F + T\,\Delta S, \tag{1}$$

in which ΔH, ΔF, and ΔS represent the changes in total energy, free energy, and entropy, respectively, while T is the absolute temperature at which the reaction takes place. This equation, a statement of the second law of thermodynamics, means that the total energy change (as represented by the heat of the reaction) includes the free-energy change (energy available for doing external work in a process occurring at constant temperature and pressure) plus the quantity $T\ \Delta S$, which is the irreversible energy represented by heat that must be absorbed from or given up to the surroundings during the reversible process in order that the process may occur without change of temperature. ΔH may be either greater or less than ΔF, depending on whether the heat is absorbed or given up.

In order to visualize the relation between heat of reaction and free energy, let a and b represent molal quantities of two substances. Let these react to form molal quantities of two other substances, c and d. The reaction would be written

$$a + b = c + d.$$

Let the reaction take place in a calorimeter, and measure the quantity of heat produced by it. Determine this quantity of heat under the condition of no change in temperature, *i.e.*, the temperature of c and d after the reaction being the same as that of a and b before the reaction. The quantity so determined is the heat of the reaction. Obviously this is a quantity illustrated by the calorific power of a fuel, the heat absorbed in reducing Fe_2O_3 to Fe, or any of the heats of formation or reaction which properly form the basis of calculations of heat requirements or heat balances.

Now note that c and d are different substances from a and b; it would require a different amount of heat to bring them from the temperature of absolute zero to the temperature at which they reacted or were formed in the calorimeter. If the sensible-heat capacity of c and d is less than that of a and b, the disappearance of a and b would liberate more heat than c and d would absorb and consequently part of the heat measured in the calorimeter would have come from this source and not from the latent heat of the reaction. If the heat capacity of c and d is greater than that of a and b, some of the heat change inherent in the reaction would not actually be given out in the calorimeter but would be taken up by c and d. In the latter case, the heat of the reaction would have been less than this inherent heat change; in the former case the heat of the reaction would have been greater than this inherent heat change. This inherent heat change is the free-energy change, and it clearly differs in amount from the total energy change (heat of reaction) as measured in the calorimeter. The amount by which it differs is thus related to the difference between the heat capacities of the reactants and those of the products, a difference which we may denote by ΔC_p. This relation, however, is not one which can be expressed by a simple algebraic difference or which can be readily visualized, since it is not the difference between the heat capacities at any one temperature. It is an integrated sum of all the infinitesimal differences between the heat capacities as the temperature changes from 0 to T. The relation can only be precisely expressed mathematically; it is given by the equation

$$\Delta H = \Delta F + T \int_0^T \frac{\Delta C_p}{T}\, dT, \tag{2}$$

which is equivalent to Eq. (1). Calling the entropy change ΔS, we may write:

$$\Delta F = \Delta H - T\,\Delta S,$$

in which

$$\Delta S = \int_0^T \frac{\Delta C_p}{T}\, dT. \tag{3}$$

From the electrochemical viewpoint, it has been pointed out in Chap. XVI, page 264, that the available energy derived as e. m. f. in a voltaic cell does not equal the total energy change indicated by the heat of reaction of the cell but differs from this total energy change by an amount equal to the temperature coefficient of the cell multiplied by its absolute temperature; thus:

$$E = \frac{-\Delta H}{23{,}060n} + T\frac{dE}{dT}. \tag{4}$$

The temperature coefficient $\frac{dE}{dT}$ may be either positive or negative. If it is considered negative in the equation, this means that, of the total decrease of energy suffered by the reacting components of the cell when the cell is supplying electrical energy, only part is obtained as available electrical energy; the rest appears as heat which goes to raise the temperature of the components of the cell. If it is considered positive, it means that the available electrical energy obtained is greater than that derived from the total decrease of energy of the system, the extra amount being extracted from the sensible-heat contents of the components of the cell and causing their temperature to fall. In a reversible electrolytic cell:

$$nF\frac{dE}{dT} = \Delta S. \tag{5}$$

It is the free-energy change rather than the heat of a reaction which determines the driving force behind the reaction. Just as, in Eq. (4),

E and not ΔH measures the potential of the cell, so ΔF and not ΔH measures the chemical driving force in a reaction. It is the free energy, therefore, which must be used in determining such questions as whether any particular reaction will go from right to left, or vice versa, under given conditions of temperature and pressure, or how far (*i.e.*, to what relative concentrations of reagents and products) a given reaction will proceed, or in general any questions involving equilibrium.

Practical examples of questions of this kind are: To what extent is it possible to remove carbon from iron by Fe_2O_3 in the open-hearth furnace? What concentration of CO would be necessary to reduce ZnO to Zn at a given temperature and pressure? Experience in purification of pig iron indicates that at low furnace temperatures phosphorus is oxidized more readily than carbon, while at high furnace temperatures the reverse is the case. The relative heats of formation are not true criteria of the comparative ease of oxidation; the free-energy changes are. Free-energy equations would express the relations definitely as functions of temperature and permit calculation of the intermediate temperature at which phosphorus and carbon have equal affinities for oxygen.

Free Energy and Thermodynamic Potential.—The foregoing discussion of the relation between heat of reaction and free energy has avoided the question of expenditure of energy corresponding to $p\ \Delta v$ when the reaction is accompanied by change of volume, as in the frequent case of a gas being produced from solid reacting substances. In this case a portion (usually relatively small) of the energy change is used in doing the work of volume increase against the opposing pressure. When Helmholtz introduced the term "free energy" (1882), he assigned it to the maximum work at constant volume. Gibbs gave a different name to the maximum work at constant pressure, calling it the "thermodynamic potential" (1873).

If a, b, c, and d in the above equation (page 374) are all solids or liquids, change of volume is negligible and no distinction between free energy and thermodynamic potential is necessary. But if a gas is liberated with increase of volume, it is the diminished free energy or thermodynamic potential which determines the driving force of the reaction.

Some writers, recognizing that the function called "free energy" by Helmholtz is not the determining one in cases of equilibrium where the distinction is involved, have reserved the term "free energy" (F) for the thermodynamic potential and have practically abandoned use of the latter term. The Helmholtz type of free energy they call the "maximum work at constant volume" (A). This terminology has been widely adopted. Using the sign convention that liberation of energy (or decrease of energy suffered by the reacting system) is called negative, we then have:

$$F = A + pv. \tag{6}$$

CALCULATION OF FREE-ENERGY CHANGE

Determination of Free-energy Change from Reaction Potential.—From the discussion of Eq. (4) above, it is evident that the reaction voltage of a cell is a direct measure of the free-energy change of the chemical reaction of the cell. This provides a convenient and accurate means of finding the free-energy change of a reversible reaction that can be carried out in an electrolytic cell:

$$-\Delta F = 23{,}060nE, \tag{7}$$

where ΔF is in calories, n is the number of chemical equivalents involved, and E is the reaction potential in volts. Unfortunately, relatively few reactions can be carried out in this manner.

Free-energy Equations.—A more general method of determining free-energy change rests on its relation to heat of reaction, as discussed on page 375. This relation is expressed in Eq. (2), which may be written:

$$\Delta F = \Delta H_T - T \int_0^T \frac{\Delta C_p}{T}\, dT. \tag{8}$$

In this equation ΔH_T is the heat of the reaction at T°K., and ΔC_p is the difference between the heat capacities of the reactants and the products.

The use of Eq. (8) requires integration of the expression for change of heat capacity. The specific heat of each substance in the reaction, per mol of substance, must be known and should be expressed in the general form

$$C_p = \Gamma_0 + \Gamma_1 T + \Gamma_2 T^2 + \cdots, \tag{9}$$

where Γ_0 is the specific heat at 0°K. and Γ_1, Γ_2, etc., are constants giving the increase of the specific heat with temperature. The difference between the specific heats of the reactants and products, denoted by ΔC_p, is then:

$$\Delta C_p = \Delta\Gamma_0 + \Delta\Gamma_1 T + \Delta\Gamma_2 T^2 + \cdots. \tag{10}$$

This expression is found directly by simple addition and subtraction of the values of C_p for the different substances.

From Eqs. (8) and (3), using for clarity the symbol Q_T instead of ΔH_T, we have:

$$\frac{\Delta F}{T} = \frac{Q_T}{T} - \Delta S. \tag{11}$$

By differentiation,[1]

$$\frac{d(\Delta F/T)}{dT} = -\frac{Q_T}{T^2}. \tag{12}$$

To obtain the heat of reaction at any temperature T, Eq. (10) must be integrated and added to ΔH_0, giving:

$$\Delta H_T = \Delta H_0 + \Delta\Gamma_0 T + \tfrac{1}{2}\Delta\Gamma_1 T^2 + \tfrac{1}{3}\Delta\Gamma_2 T^3 + \cdots. \tag{13}$$

Substituting this value of ΔH_T for Q_T in Eq. (12) and integrating, we have

$$\frac{\Delta F}{T} = \frac{\Delta H_0}{T} - \Delta\Gamma_0 \ln T - \tfrac{1}{2}\Delta\Gamma_1 T - \tfrac{1}{6}\Delta\Gamma_2 T^2 - \cdots + I,$$

or

$$\Delta F = \Delta H_0 - \Delta\Gamma_0 T \ln T - \tfrac{1}{2}\Delta\Gamma_1 T^2 - \tfrac{1}{6}\Delta\Gamma_2 T^3 - \cdots + IT. \tag{14}$$

Equation (14) is the general form of the free-energy equation. It gives the relation between the free-energy change and temperature, so that ΔF may be calculated for any desired temperature.

In order to apply Eq. (14), it is necessary to determine the value of the integration constant I. This can be done if the heat of reaction is known at any temperature, ΔH_0 being thus obtained from Eq. (13), and if the value of ΔF is known at some temperature. Under the condition of equilibrium, the driving force of a reaction in the left-right direction is exactly balanced by the driving force in the right-left direction; in other words, $\Delta F = 0$. This gives a known value of ΔF when the temperature of equilibrium is known. When the value of ΔF is not obtainable in this way, it may often be found from the relation

$$\Delta F^\circ = -RT \ln K, \tag{15}$$

where K is the equilibrium constant for the reaction, derivable from the relation $K = \frac{[c] \times [d]}{[a] \times [b]}$ at temperature T.

Necessary Data.—For the determination of the free-energy equation of a given reaction, it is seen that the following data are required:

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[1] The details are as follows: Differentiating Eq. (11) with respect to T:

$$\frac{d(\Delta F/T)}{dT} = \frac{T(dQ_T/dT) - Q_T}{T^2} - \frac{d\,\Delta S}{dT}$$

$$= -\frac{Q_T}{T^2} + \left(\frac{dQ_T/dT}{T} - \frac{d\,\Delta S}{dT}\right).$$

The term in parenthesis becomes zero, for $\frac{d\,\Delta S}{dT} = \frac{\Delta C_p}{T}$, and $\Delta C_p = \frac{dQ_T}{dT}$.

1. The specific heats of all the substances involved, including the constants giving variation of the specific heat with temperature when it so varies.
2. The heat of the reaction at some known temperature.
3. A single pair of values of the free-energy change and temperature. This last may require knowledge of (*a*) the voltage of a cell in which the reaction is carried out, (*b*) a temperature of equilibrium, or (*c*) a value of K, the equilibrium constant.

Since Eq. (8) above may be written

$$\Delta F = \Delta H - T\,\Delta S, \tag{16}$$

in which ΔS is the entropy change of the reaction, a pair of values of ΔF and T may also be obtained by reference to tables giving entropy values, when these values are available for the substances involved. The entropy of the reaction is obtained by addition and subtraction of the entropies of the different substances in the reaction, just as in finding the heat of a reaction from the heats of formation of the different substances. Many entropy values have been determined and tabulated in the past few years, so that Eq. (16) is now readily usable in many problems.

Equations (7), (15), and either (8) or (16) represent three different methods of calculating free-energy changes. A fourth method, which will not be discussed here and is at present less frequently applicable, is based on the use of spectroscopic data.

Standard Free-energy Equation.—When the temperature or other conditions under which a reaction takes place are such that one or more of the substances have undergone a change of state, or other physical change, as compared with what may be regarded as the normal standard state at room temperature, the standard free-energy change, denoted by ΔF°, must take this physical change into account. This can be done in some cases by including all the heats of transition that accompany the changes of state in the right-hand side of Eq. (8). For gases and solutions, the relation is:

$$\Delta F = \Delta F^\circ + RT \ln a, \tag{17}$$

where a is the "activity quotient." However, this is usually unnecessary, since tables give directly the values of ΔF° for the formation of substances in their standard states.

Standard free-energy equations can be added and subtracted in the same manner as thermochemical equations (see page 82). This permits the finding of many unknown free-energy values from known ones.

Example 46

1. Calculate the free-energy equation for the reaction

$$H_2 + \frac{1}{2}O_2 = H_2O(g).$$

2. What is the value of the free-energy change when the reaction takes place at 27° and at 1000°C.?

3. Calculate the free-energy change at 27°C. for the reaction

$$H_2 + \frac{1}{2}O_2 = H_2O(l).$$

Solution: At 18°C., $H_2 + \frac{1}{2}O_2 = H_2O(g)$; $\Delta H = -57{,}801$ cal. Therefore, $\Delta H_T = \Delta H_{291} = -57{,}801$.

The specific heats of the three gases, given at the foot of Table XV, page 393, per liter and with 0°C. as a base, must be expressed per mol and with 0°K. as base and as actual, not mean, specific heats. We then have:

For H_2:

$$C_p = 6.85 + 0.00028T + 0.00000022T^2 \ (a).$$

For $\frac{1}{2}O_2$:

$$C_p = \frac{1}{2}(6.76 + 0.000606T + 0.00000013T^2) \ (b).$$

For H_2O:

$$C_p = 8.22 + 0.00015T + 0.00000134T^2 \ (c).$$

Taking $-(a) - (b) + (c)$:

$$\Delta C_p = -2.01 - 0.000433T + 0.000001055T^2$$

Using Eq. (13) above:

$$\Delta H_0 = -57{,}801 + 291(2.01 + 0.000216 \times 291 - 0.000000352 \times 291^2) = -57{,}206 \text{ cal.}$$

By Eq. (14):

$$\Delta F = -57{,}206 + 2.01T \ln T + 0.000216T^2 - 0.00000018T^3 + IT.$$

Evaluation of the constant I:

This requires a single pair of values for ΔF and T A pair of values may be obtained from any value of the equilibrium constant K in the relation

$$K = \frac{[H_2O]}{[H_2][O_2]^{\frac{1}{2}}}$$

at a known temperature T, as derived from pressure measurements of the reaction

$$H_2O = H_2 + \frac{1}{2}O_2$$

at high temperature, giving the amount of dissociation of water vapor. Since experimental determinations of this dissociation are not easy, there is some variation in available data. The most reliable value of I would be obtained by determining I from a number of such determinations and then finding the mean. The purpose of this illustrative example, however, will be served by using a single determination; one will be selected that is known to yield a value close to the mean.

Von Wartenberg found that H_2O was 1.77 per cent dissociated at 1984°C. (2257°K.); *i.e.*, of every 100 mols of H_2O, 1.77 broke down, giving 1.77 mols of H_2 and 0.885 mol of O_2 and leaving 98.23 mols of H_2O. Then at this temperature:

$$K = \frac{0.9823}{0.0177 \times \sqrt{0.00885}} = 590.$$

By Eq. (15):

$$\begin{aligned} \Delta F^\circ &= -RT \ln 590 \\ &= -1.9885 \times 2257 \times 2.3026 \times 2.771 \\ &= -28{,}650 \text{ cal}, \text{ at } 2257^\circ\text{K} \end{aligned}$$

Then:

$$-28{,}650 = -57{,}206 + 2.01 \times 2{,}257 \times 2.3026 \times \log 2{,}257 + 0.000216 \times 2{,}257^2 - 0.00000018 \times 2{,}257^3 + 2{,}257I,$$

whence

$$I = -2.439$$

The free-energy equation then is

$$\Delta F = -57{,}206 + 2.01T \ln T + 0.000216T^2 - 0.00000018T^3 - 2.439T \quad (1).$$

At 27°C., $T = 300$ Then $\Delta F = -54{,}485$ cal.

At 1000°C., $T = 1{,}273$. Then $\Delta F = -42{,}039$ cal (2)

The free-energy change for formation of liquid water may be obtained by subtracting from ΔF_{300} above the free-energy change of vaporization of water at 27°C. The latter can be obtained directly from the vapor pressure at 27°C., which is 26.7 mm.:

$$\begin{aligned} \Delta F = -RT \ln \left(\frac{26.7}{760}\right) &= -1.9885 \times 300 \times 2.3026 \times (-1.455) \\ &= 1{,}999 \text{ cal}. \end{aligned}$$

Then, $-54{,}485 - 1{,}999 = -56{,}484$ cal. is the free-energy change in formation of liquid water at 27°C. (3).

In performing the computations necessary for calculating free-energy change, as in the foregoing example, one must exercise care with respect to the signs. When a reaction evolves heat, ΔH is negative; accordingly, in obtaining ΔC_p, the heat content of the reacting substances, which is liberated when they disappear, is also negative, and that absorbed by the products is positive. The sum of these positive and negative quantities (equivalent to the heat content of the products minus the heat content of the reactants) is added to ΔH_0 to obtain ΔH_T (or subtracted from ΔH_T to obtain ΔH_0).

The accuracy of available data for most reactions would not justify carrying the number of figures carried in Example 46.

The use of Eq. (16) is a very simple method of obtaining ΔF_T for any reaction when ΔH_T is known and ΔS_T can be obtained from the entropies of the substances in the reaction. These entropies may be looked up in tables and summated to obtain ΔS in the same manner as the heats of formation are summated to obtain ΔH. The value thus obtained for ΔF_T, however, holds only for the temperature T, which would be the same as in ΔS_T and therefore limited to the temperature specified in the entropy tables. For ΔF at other temperatures it would then be necessary to obtain the free-energy equation [Eq. (14)] for the reaction.

APPLICATIONS OF THERMODYNAMIC DATA

Equations (7) and (15) show the possibility of using free-energy values to calculate cell potentials and equilibrium constants. In Chap. XXIII we have noted also its use in obtaining the constants in the accurate forms of the vapor or reaction temperature-pressure equations. The use of ΔF in solving problems of equilibrium and some practical examples have been noted on page 218.

In addition to these applications, it may be noted that no chemical reaction can occur spontaneously under a given set of conditions unless there is a positive driving force behind it, *i.e.*, unless there is a positive decrease of free energy (thermodynamic potential) in the reaction, which means that ΔF must be negative. The more positive ΔF becomes, the more energy must be supplied to make the reaction go in the left-right direction. If the conditions change so that the system approaches equilibrium, ΔF approaches zero.

The values of ΔF and ΔH for a given reaction in general approach each other as the temperature is lowered and become equal at absolute zero. At absolute zero the heat capacity C_p, the entropy S, the heat content, and the free-energy content of a substance are all zero.

It is important to note that free-energy values give information on equilibrium, for example, as to how far a reaction will go under given conditions, but do not tell anything regarding reaction rates.

Practical use of the methods of thermodynamics in metallurgy has not as yet been extensive, but it is receiving more and more attention. Further impetus has been given to it in the past few years by determination of many of the necessary fundamental data on heat capacities, heats of formation, free energies, and entropies and the compilation of these in readily available form. In addition to the pioneer work of Lewis and Randall, the work of the U.S. Bureau of Mines at the Pacific Experiment Station and its series of *Bulletins* entitled "Contributions to the Data on Theoretical Metallurgy" may be specially mentioned.

Literature

The following list of books includes some which discuss the principles involved and some which give tabulated data needed in thermodynamic calculations:

BICHOWSKY, F. R., and F. D. ROSSINI: "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corporation, New York, 1936.

"International Critical Tables," Vols. V and VII, McGraw-Hill Book Company, Inc., New York, 1929–1930.

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LEWIS, GILBERT N., and MERLE RANDALL: "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, 1923

MAIER, C. G.: "Zinc Smelting from a Chemical and Thermodynamic Viewpoint," *U.S. Bur. Mines, Bull* 324, 1930.

NOYES, A. A., and M. S. SHERRILL: "Course of Study in Chemical Principles," 2d ed., The Macmillan Company, New York, 1938.

PARTINGTON, J. R.: "Chemical Thermodynamics; an Introduction to General Thermodynamics and Its Applications to Chemistry," 2d ed., Constable & Company, Ltd., London, 1940.

TAYLOR, H. S., and S. GLASSTONE, (editors): "A Treatise on Physical Chemistry," 3d ed., Vol. I, "Atomistics and Thermodynamics," D. Van Nostrand Company, Inc., New York, 1942.

THOMPSON, M. DE K.: "The Total and Free Energies of Formation of the Oxides of Thirty-two Metals," The Electrochemical Society, Inc., New York, 1942.

WENNER, RALPH R.: "Thermochemical Calculations," McGraw-Hill Book Company, Inc., New York, 1941.

CHAPTER XXV

TABLES

The tables following are designed to supply the data necessary for solution of ordinary problems in metallurgy; they are given in a form convenient for use in the classroom and other places where reference books are not at hand. They are made up of selected data, excluding, for the most part, figures for the rarer elements and for compounds less commonly used in metallurgy. They are not designed to replace the use of a good handbook, and it is hoped that they may encourage the student to become familiar with the large reference works of physical and chemical data.

Most of the tables are new in the sense that the data are collected and presented in a form not available elsewhere and that an effort has been made to give the most recently determined, or at least the most reliable, values. All the data, however, have been previously published, and most of them in works of reference, although a few additions have been made from other reliable publications.

Much of the work of compilation has required conversion to units other than those used in the sources. Scientific tables often employ such units as the mol and the joule; and while there is good reason for the use of such units, it has seemed preferable in this book to use those more commonly employed in practice.

The principal source of data for each table is noted with the tables individually. In many cases, however, items have been added from other sources which could not be conveniently noted at each point; instead, the words "largely from" have been inserted before the name of the principal reference; a list is given on p. 385 of the principal publications from which such added data have been obtained. This list will serve, not only as an acknowledgment, but also as a partial list of reference works for the student of the subject. It has seemed best not to enlarge the tables by giving the names of the observers of data or references to the original articles in the literature. This is commonly done in the large reference works, and it is thought that anyone desiring to make a critical examination of data would always go to them.

The "International Critical Tables" (E. W. Washburn, editor in chief, McGraw-Hill Book Company, Inc., New York, Vols. I to VII, 1926 to 1930) have been used for a considerable portion of the material.

"Physikalisch-chemische Tabellen" (Landolt-Börnstein, 1923; 1st Ergänzungsband, W. A. Roth and K. Scheel, 1927; 2d Ergänzungsband, 1931; Verlag Julius Springer, Berlin) have also been an important source.

The following works have been used either for lesser amounts of data or for purposes of comparison:

"Anhaltszahlen fur den Energieverbrauch in Eisenhüttenwerken," Warmestelle Dusseldorf des Vereins deutscher Eisenhuttenleute, 3d ed., Verlag Stahleisen m. b. H., Düsseldorf, 1931.

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Partington, J. R., and W. G. Shilling: "The Specific Heats of Gases," Ernest Benn, Ltd., London, 1924.

Richards, Joseph W.: "Metallurgical Calculations," 4th (one-volume) ed., McGraw-Hill Book Company, Inc., New York, 1918.

Sauerwald, F.: "Physikalische Chemie der metallurgischen Reaktionen," Verlag Julius Springer, Berlin, 1930.

Journal of the American Chemical Society, Easton, Pa.

Transactions of the Electrochemical Society, Columbia University, New York.

Tables I to X have appeared in the text.

TABLE XI.—SPECIFIC GRAVITY OF METALS AND OTHER MATERIALS[1]

A. Metals

Metal	Symbol	Solid		Liquid, near freezing point
		Values for non-porous metal[2]	Lower value, e g., cast metal	
Aluminum	Al	2.70	2.68	2.38
Antimony	Sb	6.71	6.62	6.41
Arsenic	As	5.73	5.71	5.71
Barium	Ba	3.7	3.6	
Beryllium	Be	1.93	1.84	
Bismuth	Bi	9.92	9.74	10.04
Cadmium	Cd	8.70	8.60	7.99
Calcium	Ca	1.55		
Cerium	Ce	6.8		
Chromium	Cr	7.1	7.0	
Cobalt	Co	8.92	8.50	8.72
Copper	Cu	8.94	8.7	8.22
Gold	Au	19.37	19.25	19.20
Iridium	Ir	22.42		
Iron	Fe	7.88	7.3	7.13
Lead	Pb	11.35		10.88
Lithium	Li	0.59	0.53	
Magnesium	Mg	1.74		1.57
Manganese	Mn	7.39		
Mercury	Hg	15.63		13.59
Molybdenum	Mo	10.2		
Nickel	Ni	8.91	8.85	8.79
Osmium	Os	22.48		
Palladium	Pd	12.16		
Platinum	Pt	21.7	21.1	21.3
Potassium	K	0.875		0.83
Rhodium	Rh	12.50	12.40	
Selenium	Se	4.8 (metallic)	4.47 (red)	3.98
Silicon	Si	2.34	2.19	
Silver	Ag	10.75	10.50	9.27
Sodium	Na	0.972		0.93
Strontium	Sr	2.54		
Tantalum	Ta	16.6		
Tellurium	Te	6.25		
Tin	Sn	7.30	7.28	6.98
Titanium	Ti	4.5		
Tungsten	W	20.2	19.1	
Uranium	U	18.69		
Vanadium	V	5.7	5.50	
Zinc	Zn	7.13	7.0	6.92

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[1] These values give also the density in grams per cubic centimeter; for the distinction between specific gravity and density, see p. 3.

[2] Use these values for rolled metal and for commercial deposits of electroplated or electrolytically refined metal.

TABLE XI.—SPECIFIC GRAVITY OF METALS AND OTHER MATERIALS.—(*Concluded*)
B. Other Elements, Alloys, Compounds, Etc.[3]

Metal	Symbol	Solid		Liquid, near freezing point
		Nonporous	Lower value	
Alumina	Al_2O_3	4.00	3.75	
Boron	B	2.45		
Brass (70–30)		8.4	7.8	
Bronze		8.9	8.7	
Cast iron		7.6 (white)	7.08 (gray)	6.88
Cement, set		3.0	2.7	
Cementite	Fe_3C	7.66		
Charcoal		0.21		
Clay		2.6	1.8	
Coal, anthracite		1.7	1.3	
Coal, bituminous		1.5	1.2	
Concrete		2.3		
Copper aluminide	$CuAl_2$	4.2		
Cork		0.24		
Gasoline				0.70
Glass		2.52		
Gold, coin		16.95		
Graphite		2.25		
Iron oxide	Fe_2O_3	5.3	5.2	
Lime	CaO	3.3		
Limestone		2.7		
Manganin		8.42		
Mica		2.8		
Monel metal		8.80		
Nickel silver		8.45		
Pearlite	$Fe\text{-}Fe_3C$	7.83		
Petroleum				0.77–1.06
Phosphorus	P	2.34 (red)	1.84 (white)	1.75
Rubber		1.40	1.12	
Silica, fused	SiO_2	2.21	2.10	
Silica, sandstone	SiO_2	2.70	2.10	
Silicon carbide	SiC	3.12		
Slate		2.9	2.7	
Soda ash	Na_2CO_3	1.2		
Steel, high speed		8.64	8.32	
Steel, mild		7.93	7.69	
Stellite		8.54		
Sulphur	S	2.07	1.96	1.81
Tar		1.0		
Tungsten carbide	WC	14.5		
Water	H_2O	0.92		1.00
Wrought iron		7.9	7.6	

[3] Largely from LIDDELL, DONALD M., "The Metallurgists' and Chemists' Handbook," 3d ed., McGraw-Hill Book Company, Inc., New York, 1930.

TABLE XII.—MELTING AND BOILING POINTS AND HEATS OF FUSION AND VAPORIZATION*

(Temperatures in degrees centigrade; heats in gram-calories per gram, kilogram-calories per kilogram, or pound-calories per pound)

Element	Symbol	Melting point	Normal boiling point	Latent heat of fusion	Latent heat of vaporization†
Aluminum	Al	659	2060	94.5	2,260
Antimony	Sb	630	1440	39.2	383
Arsenic	As		610‡	. .	103‡
Barium	Ba	710	1630	17	260
Beryllium	Be	1278	3040	345	8,440
Bismuth	Bi	271	1420	12.0	230
Boron	B	2300	2600	265	4,150
Cadmium	Cd	321	765	13.0	212
Calcium	Ca	851	1480	56	914
Carbon	C	.	3700‡	. .	10,800‡
Cerium	Ce	775	1400	15.1	
Cesium	Cs	29	690	3.8	123
Chlorine	Cl	−101	−35	22.8	69
Chromium	Cr	1550	2480	76	1,470
Cobalt	Co	1490	3100	62	1,250
Copper	Cu	1084	2595	57.6	1,150
Fluorine	F	−223	−188	10.1	43
Gallium	Ga	30	2070	19.1	
Gold	Au	1063	2966	15.4	415
Hydrogen	H	−259	−253	13.9	200
Indium	In	157	1450	6.8	
Iodine	I	113	183	14.4	41
Iridium	Ir	2454	4900	28	370
Iron	Fe	1534	3000	64.9	1,515
Lead	Pb	327	1740	5.9	203
Lithium	Li	179	1370	158	4,650
Magnesium	Mg	650	1110	89	1,340
Manganese	Mn	1220	2150	63	1,000
Mercury	Hg	−39	357	2.78	70
Molybdenum	Mo	2622	4800	70	1,340
Nickel	Ni	1455	2730	72	1,490
Nitrogen	N	−210	−196	6.2	48
Osmium	Os	2700	5000	40	450
Oxygen	O	−219	−183	3.3	51
Palladium	Pd	1556	3800	38.6	670
Phosphorus (yellow)	P	44	280	4.8	101
Platinum	Pt	1773	4400	24.1	548
Potassium	K	64	774	14.7	484
Rhodium	Rh	1966	4300	53	680
Rubidium	Rb	39	679	6.1	212
Ruthenium	Ru	2450	4500	46	700
Selenium	Se	217	680	15.4	161
Silicon	Si	1427	2290	337	1,400
Silver	Ag	961	2210	25.0	563
Sodium	Na	98	892	27.4	1,005
Strontium	Sr	757	1380	25	384
Sulphur	S	119	445	9.2	79
Tantalum	Ta	3027	4200	37	
Tellurium	Te	453	1090	25.3	210
Thallium	Tl	303	1460	5.0	190
Thorium	Th	1845	3000	18	
Tin	Sn	232	2270	14.5	143
Titanium	Ti	1800	3000	90	145
Tungsten	W	3387	5900	46	960
Uranium	U	1688	2900	20	330
Vanadium	V	1710	3000	80	
Zinc	Zn	419	905	24.4	426
Zirconium	Zr	1857	2900	60	
		Alloys			
Cast iron, gray		1150–1200	. . .	56	
Cast iron, white		1350–1400	. .	54	
Pig iron, 4.34% C		1150		59	
Monel metal		1300–1350		68	
Brass		850–1000			
Bronze		700–900			
Stellite		1275			
Duralumin		650			
$CuAl_2$		590		74	

TABLE XII.—MELTING AND BOILING POINTS AND HEATS OF FUSION AND VAPORIZATION.*—(*Concluded*)

Compound	Symbol	Melting point	Normal boiling point	Latent heat of fusion	Latent heat of vaporization†
		Compounds			
Alumina	Al_2O_3	2045	2980	250	1,270
Aluminum chloride	Al_2Cl_6	.	180‡	.	100‡
Ammonia	NH_3	−78	−33	79	328
Antimony trioxide	Sb_4O_6	655	1425	46	31
Arsenic trioxide	As_4O_6	313	457	20.2	77
Beryllium chloride	$BeCl_2$	405	488		
Cadmium oxide	CdO	.	1560‡	...	420‡
Calcium fluoride	CaF_2	1392	. .	53	
Calcium oxide	CaO	2710	..	220	
Carbon dioxide	CO_2		−78‡	..	139‡
[illegible]	Cu_2Cl_2	430	1490	25	60
[illegible]	Cu_2O	1230	.	95	
[illegible]	CuO	1447		35.5	
[illegible]	Cu_2S	1127		34.5	
[illegible]	Na_3AlF_6	1000	.	79.2	
Iron chloride	$FeCl_2$	677	1026	62	238
Iron oxide	FeO	1380	....	110	
Iron sulphide	FeS	1195		57	
Lead chloride	$PbCl_2$	498	954	20.3	106
Lead oxide	PbO	890	1470	12.6	230
Lead sulphate	$PbSO_4$	1087	.....	32	
Lead sulphide	PbS	1114	1281	17.3	
Magnesium chloride	$MgCl_2$	712	1418	85	340
Magnesium fluoride	MgF_2	1221	...	95	
Nickel sulphide	Ni_3S_2	790		24	
Potassium chloride	KCl	770	1407	86	520
Potassium nitrate	KNO_3	338		28.1	
Selenium dioxide	SeO_2	.	317‡	.	188‡
Silica (quartz)	SiO_2	1470	2230	57	
Silica (cristobalite)	SiO_2	1700	2230	35	
Silicates	$CaAl_2Si_2O_8$	1550	.	106	
	$CaMgSi_2O_6$	1392		84	
	$CaSiO_3$	1510		115	
	Fe_2SiO_4	1210		85	
	$KAlSi_3O_8$	.		83	
	$MgSiO_3$	1524		147	
	$NaAlSi_3O_8$	1107	.	50	
	Na_2SiO_3	1087		84	
Silver chloride	AgCl	455	1560	22.0	
Silver nitrate	$AgNO_3$	209	....	16.2	
Silver sulphide	Ag_2S	892	...	13.6	
Sodium chloride	NaCl	800	1465	124	700
Sodium fluoride	NaF	992	1700	167	1,270
Sodium hydroxide	NaOH	322	1374	50	
Sodium nitrate	$NaNO_3$	310	.....	44	
Sulphur dioxide	SO_2	−73	−10	43	133
Tin chloride	$SnCl_4$	−33	113	8.4	32
Titanium oxide	TiO_2	1825	.....	143	
Water	H_2O	0	100	79.7	539
Zinc chloride	$ZnCl_2$	283	722	41	210
Zinc oxide	ZnO	1975	.	55	
Zinc sulphide	ZnS	1645		93	

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* Largely from KELLEY, K. K., "Contributions to the Data on Theoretical Metallurgy," Nos. III and V, *Bulls* 383 (1935) and 393 (1936). Some figures also from "International Critical Tables" and "Physikalisch-chemische Tabellen."

† At the boiling point, under normal atmospheric pressure.

‡ Sublimation.

TABLE XIII.—LATENT HEATS OF TRANSFORMATION[1]

(Temperatures in degrees centigrade, heats in gram-calories per gram, kilogram-calories per kilogram, or pound-calories per pound)

Element	Symbol	Transformation	Temperature	Latent heat
Iron	Fe	A_2	769	0 0
Iron	Fe	$\alpha \rightarrow \gamma$ (A_3)	910	3 86
Iron....	Fe	$\gamma \rightarrow \delta$ (A_4)	1400	1 86
Manganese	Mn	$\alpha \rightarrow \beta$	1070–1130	24 1
Nickel	Ni	$\alpha \rightarrow \beta$	352	1 33
Tin ...	Sn	White → gray	0	4 46

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[1] Data on iron from "The Metal—Iron," by H. E. Cleaves and J. G. Thompson, McGraw-Hill Book Company, Inc., New York, 1935. Other data from "International Critical Tables," Vol II, 1927.

TABLE XIV.—SPECIFIC HEATS OF ELEMENTS IN THE SOLID, LIQUID, AND VAPOR STATES, AND TOTAL HEAT CONTENTS ABOVE 0°C. AT THEIR MELTING AND BOILING POINTS[1]

(In kilogram-calories per kilogram, gram-calories per gram, or pound-calories per pound)

c_m = mean specific heat between 0 and t°C.

Q_{LMP} = total heat content of liquid at the melting point, using 0°C. as a base line (*i.e.*, in excess of the heat content at 0°C.). Subtracting the latent heat of fusion (Table XII) from the figures in this column gives the heat content of the solid at the melting point on the same basis.

Q_{VBP} = total heat content of the vapor at the normal boiling point, using 0°C. as a base line. Subtracting the latent heat of vaporization (Table XII) gives the heat content of the liquid at the boiling point on the same basis.

Element	Symbol	c_m, solid[2]	Melting point	Q_{LMP}	c, liquid[5]	Normal boiling point	Q_{VBP}[3]	c, vapor[4,5]
Aluminum	Al	$0.218 + 0.000,048t$	659	240	0.26	2060	2,860	0.185
Antimony	Sb	$0.050 + 0.000,074t$	630	74	0.13	1440	562	0.025
Arsenic	As	0.082				610	153	0.040
Barium	Ba	0.068	710	65		1630		
Beryllium	Be	$0.38 + 0.000,4t$	1278	1,480	1.5	3010	12,500	0.5
Bismuth	Bi	$0.029 + 0.000,013t$	271	21	0.036	1420	292	0.024
Boron	B	$0.217 + 0.000,36t$	2300	2,660	0.6	2600	7,000	0.3
Cadmium	Cd	$0.0548 + 0.000,012t$	321	39	0.08	765	287	0.045
Calcium	Ca	$0.152 + 0.000,052t$	851	223	0.26	1480	1,300	0.12
Carbon	C	$0.206 + 0.000,178t - 0.000,000,033t^2$				3700	13,000	0.3
Cerium	Ce	0.051	775	55	0.07	1400	. .	0.036
Cesium	Cs	$0.052 + 0.000,013t$	29	5.5	$0.60 - 0.000,017t$	690	520	0.038
Chromium	Cr	$0.10 + 0.000,026t$	1550	293	0.20	2480	1,880	0.10
Cobalt	Co	$0.091 + 0.000,044t$	1490	296	0.21	3100	1,880	0.085
Copper	Cu	$0.092 + 0.000,012,5t$	1084	172	0.112	2595	1,490	0.08
Gold	Au	$0.0308 + 0.000,006,0t$	1063	55	0.041	2966	548	0.025
Iodine	I	0.052	113	20.3	0.068	183	66	0.071
Iridium	Ir	$0.032 + 0.000,006t$	2454	143	0.060	4800	660	0.02
Iron, 0–600°C	Fe	$0.101 + 0.000,064t$		85*				
Iron, 600–760°C	Fe	$0.180 + 0.000,3(t - 600)$		171*				
Iron, 760–910°C	Fe	$0.320 - 0.000,53(t - 760)$		161*				
Iron, 910–1400°C	Fe	$0.160 + 0.000,01(t - 910)$		241*				
Iron, 1400–1534°C	Fe	0.185 (constant)	1534	344	0.21	3000	1,970	0.09
Lead	Pb	$0.0302 + 0.000,006,0t$	327	16.4	0.033	1740	266	0.024
Lithium	Li	1.09	179	353	2.2	1370	7,600	0.7
Magnesium	Mg	$0.247 + 0.000,050t$	650	271	0.29	1110	1,740	0.21
Manganese	Mn	$0.11 + 0.000,10t$	1220	272	0.36	2150	1,600	0.09
Mercury	Hg	0.033	−39	2.8	0.033	357	85	0.025
Molybdenum	Mo	$0.065 + 0.000,02t$	2622	378	0.17	4800	2,090	0.05
Nickel, 0–352°C	Ni	$0.103 + 0.000,051t$						

TABLE XIV.—SPECIFIC HEATS OF ELEMENTS IN THE SOLID, LIQUID, AND VAPOR STATES AND TOTAL HEAT CONTENTS ABOVE 0°C. AT THEIR MELTING AND BOILING POINTS.[1]—(*Concluded*)

Element	Symbol	c_m, solid[2]	Melting point	Q_{LMP}	c, liquid[5]	Normal boiling point	Q_{VBP}[3]	c, vapor[4,5]
Nickel, 252–1455°C.	Ni	0.128	1455	259	0.16	2730	1,950	0.09
Osmium	Os	0.03 + 0.[illegible],[illegible]t	2700	165	0.062	5000	760	0.025
Palladium	Pd	0.058 + 0.[illegible],010t	1556	153	0.089	3800	1,020	0.05
Phosphorus	P	0.216 + 0.[illegible],22[illegible]t	44	14.8	0.23	280	170	0.097
Platinum	Pt	0.0317 + 0.[illegible],003 2t	1773	90.4	0.043	4400	756	0.025
Potassium	K	0.173 + 0.[illegible],0[illegible]t	64	25.9	0.142 + 0.000,33t	774	810	0.13
Rhodium	Rh	0.057 + 0,[illegible].01t	1966	204	0.09	4300	1,090	0.049
Rubidium	Rb	0.080 + 0.[illegible],017t	39	9.2	0.092 − 0.000,013t	679	274	0.06
Ruthenium	Ru	0.06 + 0.[illegible],01t	2450	253	0.11	4500	1,180	0.05
Selenium	Se	0.077	217	32.1	0.12	680	249	0.04
Silicon	Si	0.1725 + 0.000,064t − 0.000,000,039t^2	1427	600	0.20	2290	2,170	0.13
Silver	Ag	0.0557 + 0.000,006,7t	961	84.7	0.086	2210	755	0.046
Sodium	Na	0.282 + 0.000,23t	98	57.2	0.32	892	1,320	0.22
Sulphur	S	0.18	119	30.6	0.210 + 0.000,08t	445	193	0.134 + 0.000,023t
Tantalum	Ta	0.033 + 0.000,[illegible]t	3027	283	...	4200		
Tellurium	Te	0.048 + 0.000,[illegible],5t	453	47.7	0.051	1090	290	0.03
Thallium	Tl	0.034 + 0.000,[illegible]t	303	16.7	0.043	1460	256	0.025
Thorium	Th	0.028 + 0.000,[illegible]t	1845	97	0.06	3000	...	0.02
Tin	Sn	0.0534 + 0.000,[illegible],4t	232	27.8	0.055	2270	283	0.042
Titanium	Ti	0.142 + 0.000,[illegible]t	1800	450	0.28	3000	930	0.10
Tungsten	W	0.0273 + 0.000,[illegible],2t	3387	186	0.056	5900	1,290	0.03
Uranium	U	0.028 + 0.000,[illegible]7t	1688	93	0.05	2900	480	0.02
Vanadium	V	0.115 + 0.000,[illegible]	1710	360	0.22	3000	...	0.10
Zinc	Zn	0.0919 + 0.000,[illegible]t	419	66.4	0.1135 + 0.000,008,8t	905	553	0.077
Zirconium	Zr	0.067	1857	184	0.1	2900	. .	0.05

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[1] Specific heats largely from "International Critical Tables," Vol. I, 1926.

[2] See footnote 2, Table XV.

[3] In most cases the heat of vaporization constitutes the major part of Q_{VBP}. Since the values of the heat of vaporization are in many cases uncertain, the values in this column are correspondingly uncertain.

[4] The specific heat of any monatomic gas or vapor is approximately 5.0 cal. per mol. Metals in general are monatomic in the vapor state. All the values in this column have been calculated from the figure 5.0 cal. per mol except where the vapor of the element is known not to be monatomic.

[5] Where an expression containing t is given, the figures are for the mean specific heat between 0 and t°C. The other figures are mean values for c in the phase stated.

* Heat content of solid iron (above 0°C.) at the upper temperature given in the first column, including the small heats of transformation shown in Table XIII. The values shown for c_m are here the mean specific heats between the temperatures given in the first column.

TABLE XV.—MEAN SPECIFIC HEATS OF GASES
(Between 0 and t°C.)

Gas	Formula	c_m, by volume[1,3] (In kilogram-calories per cubic meter or gram-calories per liter at standard conditions)	c_m, by weight[2,3] (In kilogram-calories per kilogram, gram-calories per gram, or pound-calories per pound)
Air[4]		$0.302 + 0.000{,}022t$	$0.234 + 0.000{,}017{,}3t$
Ammonia	NH_3	$0.376 + 0.000{,}14t$	$0.488 + 0.000{,}18t$
Carbon dioxide[5]	CO_2	$0.406 + 0.000{,}090t$	$0.205 + 0.000{,}046t$
Carbon monoxide[4]	CO	$0.302 + 0.000{,}022t$	$0.242 + 0.000{,}018t$
Chlorine	Cl_2	$0.387 + 0.000{,}007t$	$0.122 + 0.000{,}002{,}2t$
Ethylene	C_2H_4	$0.46 + 0.000{,}3t$	$0.37 + 0.000{,}24t$
Fluorine[4]	F_2	$0.302 + 0.000{,}022t$	$0.178 + 0.000{,}013t$
Hydrocarbons	C_xH_y	$0.20\ (x + 1) + 0.000{,}135\ (x + 2)t$, where x = no. of atoms of carbon	
Hydrochloric acid[4]	HCl	$0.302 + 0.000{,}022t$	$0.185 + 0.000{,}013t$
Hydrogen[6]	H_2	$0.301 + 0.000{,}020t$	$3.35 + 0.000{,}22t$
Hydrogen, atomic	H	0.222	4.94
Hydrogen sulphide	H_2S	$0.366 + 0.000{,}080t$	$0.240 + 0.000{,}053t$
Mercury vapor	Hg	0.222	0.0248
Methane	CH_4	$0.380 + 0.000{,}21t$	$0.53 + 0.000{,}29t$
Nitrogen[4]	N_2	$0.302 + 0.000{,}022t$	$0.241 + 0.000{,}018t$
Oxygen[4]	O_2	$0.302 + 0.000{,}022t$	$0.211 + 0.000{,}015{,}6t$
Sulphur vapor	S_2	$0.387 + 0.000{,}007t$	$0.135 + 0.000{,}002{,}4t$
Sulphur dioxide[5]	SO_2	$0.406 + 0.000{,}090t$	$0.139 + 0.000{,}031t$
Water vapor[7]	H_2O	$0.373 + 0.000{,}050t$	$0.463 + 0.000{,}062t$

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[1] This column gives the specific heat at constant pressure per unit volume referred to 0°C., 760 mm. It is equal to the molal heat capacity, C_p (more commonly given in reference tables), divided by 22.4. C_p, of course, differs considerably from C_v, the molal heat capacity at constant volume. See also footnote 3. Most of the values given in this table are derived from those given by Eastman, *U. S. Bur. Mines, Tech. Paper* 445, 1929.

[2] This column gives the specific heat at constant pressure per unit weight. It is equal to the molal heat capacity, C_p, divided by the molecular weight. See also footnote 3.

[3] The first term of the expression given represents the specific heat of the gas at 0°C.; the second term is the increment per degree, divided by 2 in order to obtain the mean between 0 and t. To find the actual specific heat at temperature t, the increment given by the second term must be doubled.

[4] The mean specific heats of air, O_2, N_2, CO, HCl, and F_2 by volume are given more accurately by the expression $0.310 + 0.000{,}015t + 0.000{,}000{,}001{,}9t^2$.

[5] The mean specific heats of CO_2 and SO_2 by volume are given more accurately by the expression $0.406 + 0.000{,}108t - 0.000{,}000{,}012t^2$.

[6] The mean specific heat of H_2 by volume is given more accurately by the expression $0.310 + 0.000{,}009{,}0t + 0.000{,}000{,}003{,}3t^2$.

[7] The mean specific heat of H_2O by volume is given more accurately by the expression $0.373 + 0.000{,}020t + 0.000{,}000{,}020t^2$.

TABLE XVI.—SPECIFIC HEATS OF ALLOYS AND VARIOUS SOLIDS[1]

(In kilogram-calories per kilogram, gram-calories per gram, or pound-calories per pound)

Substance	Specific heat	Temperature °C.
Aluminum bronze, 88.7 Cu: 11.3 Al.	0.104	20–100
92 Al: 8 Mg	0.275	18
Brass, 60 Cu: 40 Zn	0.0917	20–100
Brass, 72 Cu: 28 Zn	0.094	14– 98
Bronze, 80 Cu: 20 Sn	0.086	14– 98
Constantan	0.098–0.102	0–100
$CuAl_2$	0.1495	18–100 (mean)
$CuAl_2$	0.1610	18–600 (mean)
Cu: Sn alloys, 10–90% Cu	0.0545 + 0.00037 × % Cu	18–100 (mean)
Cu: Zn alloys, 10–90% Cu	0.0921 + 0.0000055 × % Zn	18–100 (mean)
Fe: C alloys, 0–7% C	0.1114 + 0.00440 × % C	17–100 (mean)
Pb: Sb alloys, 5–96% Sb	0.0311 + 0.000195 + % Sb	20–100 (mean)
Manganin, 84 Cu: 4 Ni: 12 Mn	0.097–0.100	0–100
Monel metal	0.127	20–400
Nickel silver.	0.094–0.095	0–100
Phosphor bronze, 88 Cu: 12 Sn: 1 P	0.0874	20–100
Solder, 63.7 Pb: 36.3 Sn	0.0407	12– 99
Solder, 46.7 Pb: 53.3 Sn	0.0451	10– 99
Asbestos.	0.195	20– 98
Cement, powder	0.20	20–100
Charcoal	0.16	10
Clay, dry	0.22	20–100
Coal.	0.24	
Glass, crown	0.161	10– 50
Glass, flint	0.117	10– 50
Granite	0.192	12–100
Ice.	0.53	– 10
Ice..	0.392	– 60
Marble..	0.21	0–100
Mica	0.206	20– 98
Porcelain....	0.26	15–950
Sand..	0.19	20–100
Wood..........	0.45–0.65	

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[1] Largely from "Handbook of Chemistry and Physics," 25th ed., Chemical Rubber Publishing Company, 1941–1942.

TABLE XVII.—MEAN SPECIFIC HEATS OF IRON-CARBON ALLOYS[1]

(In kilogram-calories per kilogram, gram-calories per gram, or pound-calories per pound)

Carbon percentage	c_m, 17–250°C.	c_m, 17–400°C.	c_m, 17–500°C.	c_m, 17–680°C.
0.17	0.118	. .	0.131	0.139
0.35	0.119			
0.45	. . . . .	0.125	0.131	0.139
0.89	0.122	0.128	0.133	0.143
1.22	. . . . .	0.130	0.134	
4.06	0.139	0.141	0.144	0.147

Heat content (above 0°C.) of pure liquid iron at the melting point = 334 cal. per gram. Specific heat of liquid = 0.21.

Heat content (above 0°C.) of liquid pig iron at the melting point = 230 cal. per gram. Specific heat of the liquid = 0.15.

[1] "International Critical Tables," Vol. V, 1929.

TABLE XVIII.—MEAN SPECIFIC HEAT OF COKE AND COKE ASH[1]

(In kilogram-calories per kilogram, gram-calories per gram, or pound-calories per pound)

Temperature range, °C.	c_m, ash (silica)	c_m, coke with ash content of:				
		5 per cent	10 per cent	15 per cent	20 per cent	25 per cent
20–100	0.190	0.193	0.193	0.193	0.192	0.192
20–200	0.204	0.225	0.224	0.223	0.222	0.220
20–300	0.217	0.252	0.250	0.248	0.247	0.245
20–400	0.227	0.277	0.275	0.272	0.269	0.267
20–500	0.235	0.297	0.294	0.290	0.287	0.284
20–600	0.242	0.313	0.309	0.306	0.302	0.298
20–700	0.247	0.327	0.323	0.318	0.314	0.310
20–800	0.250	0.337	0.333	0.328	0.324	0.319
20–900	0.253	0.347	0.342	0.337	0.332	0.327
20–1000	0.256	0.356	0.351	0.345	0.340	0.335
20–1100	0.258	0.363	0.359	0.353	0.348	0.342
20–1200	. . .	0.369	0.363	0.358	0.352	0.346

[1] From KOPPERS, in "Anhaltszahlen für den Energieverbrauch in Eisenhüttenwerken," Wärmestelle Düsseldorf des Vereins deutscher Eisenhüttenleute, 3d ed., Verlag Stahleisen m. b. H., Düsseldorf, 1931.

TABLE XIX.—MEAN SPECIFIC HEATS OF COMPOUNDS (SOLID STATE)[1]

(In kilogram-calories per kilogram, gram-calories per gram, or pound-calories per pound)

Substance	Specific heat	Temperature,[2] degrees centigrade
AgCl	0 0849	0
	0 0888	0– 100
	0 0912	0– 200
	0 0930	0– 500
Ag_2S	0 0719	0
	0 0739	0– 100
	0 0778	0– 150
$AlCl_3(\alpha)$	$0\ 157 + 0\ 000105t$	0– 193
AlF_3	0 229	0– 35
$Al(OH)_3$	0 177	0
	0 195	0– 100
	0 212	0– 800
	0 240	0–1100
Al_2O_3	$0\ 2166 + 0\ 000044T + \frac{5,126}{T^2}$	273–1973
Al_2SiO_5	0 172	0
	0 190	0– 100
	0 226	0– 800
	0 228	0–1200
As_2O_3	$0\ 109 + 0\ 000123t$	0– 275
$BaCl_2$	$0\ 0853 + 0\ 000,\ 046t$	0– 100
$BaCO_3$	0 0999	0
	0 119	0– 800
	0 130	0–1000
BeO	$0\ 347 + 0\ 000073T + \frac{12,500}{T^2}$	273–1175
Bi_2O_3	0 0569	0– 50
	0 0600	0– 300
	0 0604	0– 400
Bi_2S_3	0 0600	0– 50
CaO	$0\ 1784 + 0\ 000043T + \frac{1,926}{T^2}$	273–1173
$Ca(OH)_2$	0 260	0
	0 274	0– 50
CaF_2	$0\ 202 + 0\ 0000243t$	0–1378
$CaCl_2$	$0\ 161 + 0\ 0000174t$	0– 982
$CaSO_4$	$0\ 1693 + 0\ 000073t$	0– 400
$Ca(PO_3)_2$	0 190	0
	0 194	0– 50
CaC_2	0 220	20– 325
	0.257	20– 725
$CaCO_3$	$0\ 1968 + 0\ 0000595T + \frac{3,008}{T^2}$	273–1033
$CaSiO_3$	0 172	0
	0 215	0– 800
	0 220	0–1200
$CaMoO_4$	0 165	0– 15
$CaWO_4$	0 104	0– 15
$CaO.Al_2O_3.(SiO_2)_2$	0 174	0
	0 226	0– 800
	0 231	0–1000
CaO.MgO	0 210	0– 25
$CaCO_3.MgCO_3$	0 218	0– 46
$CaSiO_3.MgSiO_3$	0 190	0– 50
	0 237	0-1000
	0 239	0-1300
CdO	$0\ 080 + 0\ 0000081t$	0–1813
CdS	$0\ 091 + 0\ 0000031t$	0–1000
CeO_2	0 0870	0
	0 0910	0– 50
Cr_2O_3	$0\ 178 + 0\ 0000132t$	0–1990
$CuFeS_2$	0 129	0– 48
CuO	$0\ 1368 + 0\ 0000225T + \frac{1,894}{T^2}$	273– 810
Cu_3FeS_3	0 117	0– 48
Cu_2O	$0\ 101 + 0\ 000035t$	0– 600
$CuCl_2$	0 139	0– 58
CuS	$0\ 118 + 0\ 0000138t$	0–1000
Cu_2S	$0\ 0589 + 0\ 000196t$	0– 103
$CuSO_4$	0 1476	0
	0 1567	0– 50
Fe_3C	$0\ 140 + 0\ 000062t$	0– 900
FeO	$0\ 1757 + 0\ 0000104T + \frac{1,060}{T^2}$	273–1173
Fe_2O_3	$0\ 1548 + 0\ 0000502T + \frac{2,651}{T^2}$	273–1097
Fe_3O_4	$0\ 1778 + 0\ 0000406T + \frac{4,231}{T^2}$	273–1065
FeS	$0\ 1355 + 0\ 000078t$	0– 700
FeS_2	$0\ 1196 + 0\ 0000056t$	0– 500
$FeSO_4$	0 167	0– 45
$FeCO_3$	0 193	0– 54
$FeSiO_3$	0 191	0– 59
$2FeWO_4.3MnWO_4$	$0\ 098 + 0\ 000011t$	0– 300
HgO	0 0485	0
	0 0504	0– 50
HgCl	0 0500	0
	0 0506	0– 50
$HgCl_2$	0 0641	0
	0 0655	0– 100
HgS	0 0507	0
	0 0516	0– 100
KCl	0 162	0
	0 167	0– 200
	0 171	0– 400
K_2O	0 139	(Assumed)
KNO_3	0 214	0
	0 240	0– 200
	0 253	0– 300
$K_2Zn(CN)_4$	0 241	0– 30
K_2PtCl_6	0 112	0– 30
$K_2Cr_2O_7$	$0\ 178 + 0\ 000072t$	0– 400
MgO	$0\ 2693 + 0\ 0000148T + \frac{5,176}{T^2}$	273–2073

TABLE XIX.—MEAN SPECIFIC HEATS OF COMPOUNDS (SOLID STATE).[1]—(*Concluded*)

Substance	Specific heat	Temperature,[2] degrees centigrade
$MgCl_2$	$0.307 + 0.000032t$	0- 718
$MgSO_4$	0.222	0- 61
$MgCO_3$	0.200	0- 25
$Mg_3Si_4O_{11}$.- H_2O(talc)	0.208	0- 57
MnO	$0.105 + 0.00073T + \frac{51,000}{T^2}$	273-1923
MnO_2	$0.022 + 0.00027T + \frac{342,000}{T^2}$	273- 773
Mn_2O_3	$0.065 + 0.000017T + \frac{163,000}{T^2}$	273-1173
MnS	0.139	0- 30
$MnSO_4$	0.182	0- 61
MoO_4	0.134	0- 54
NaF	$0.267 + 0.000035t$	0- 988
NaCl	0.2039	0
	0.2104	0- 100
	0.216	0- 400
	0.220	0- 600
Na_2O	0.225	(Assumed)
Na_2SO_4	0.2022	0
	0.2109	0- 100
$NaNO_3$	0.247	0
	0.288	0- 200
	0.303	0- 250
$NaPO_3$	0.217	0- 30
$Na_4P_2O_7$	0.227	0- 50
Na_2CO_3	0.264	0- 98
$Na_2B_4O_7$	0.234	0- 45
$Na_2B_4O_7$ $10H_2O$ (borax)	0.385	0- 35
Na_3AlF_6	$0.1840 + 0.0001133T + \frac{2,139}{T^2}$	273-1273
NH_4Cl	0.358	0
	0.374	0- 50
NiO	$0.159 + 0.0000144t$	0-1000
NiS	$0.1212 + 0.0000353t$	0- 324
$(NH_4)_2SO_4$	0.337	0
	0.341	0- 50
$NiSO_4$	0.215	0- 58
$Ni(CO)_4$	0.165	(−78)- (−188)

Substance	Specific heat	Temperature,[2] degrees centigrade
PbO	$0.0502 + 0.0000071t$	0- 271
PbO_2	0.0619	0
	0.0634	0- 50
$PbCl_2$	0.0650	0
	0.0696	0- 300
	0.0726	0- 400
$PbCrO_4$	0.0908	0- 35
$PbSO_4$	0.0855	0- 100
PbS	$0.0490 + 0.0000084t$	0- 600
$PbCO_3$	0.0801	0- 32
$PbSiO_3$	0.0780	0- 60
Sb_2O_3	$0.082 + 0.000030t$	0- 656
Sb_2S_3	0.0830	0
	0.0845	0- 50
	0.0858	0- 100
SiO_2	See Table XX	
SiC	$0.222 + 0.0000363T + \frac{7,090}{T^2}$	273-1629
SnO_2	0.090	0- 45
$SnCl_2$	$0.0988 + 0.000244t$	0- 247
$SnCl_4$	0.14	0- 98
SnS	0.084	0- 56
ThO_2	0.0571	0
	0.0580	0- 50
ThCl	0.406	0- 30
TiO_2	$0.168 + 0.000054t$	0- 500
U_3O_8	0.0672	0
	0.0712	0- 50
WO_3	$0.0782 + 0.0000167t$	0 -1277
ZnO	$0.1149 + 0.0000267t - 0.0000000193t^2$	0-1300
$ZnCl_2$	$0.133 + 0.000030$	0- 365
ZnS	$0.1078 + 0.0000261t - 0.0000000314t^2$	0-1000
$ZnSO_4$	0.174	0- 100
$ZnSiO_3$	0.16	0
Zn_2SiO_4	0.14	0
$ZnCO_3$	$0.1537 + 0.000005t$	0- 400
ZrO_2	$0.1034 + 0.0000248t$	0-1500

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[1] In part calculated from the data given by K. K. Kelley, "High-temperature Specific-heat Equations for Inorganic Substances," *U.S. Bur. Mines, Bull.* 371 (1934), and in part from "International Critical Tables," Vol. V, 1929. (*t* represents degrees centigrade, *T* degrees Kelvin.)

[2] The values or expressions given are for the mean specific heats between the temperatures given in this column. In calculating the heat content above 0°C., when the lower limit in this column is 273°C., it is necessary to obtain the heat content at 273° (by substituting 273 for *T* in the expression given) and subtract from the heat content obtained by substituting the given temperature for *T*. (See page 88.)

Silicates: In the absence of data the specific heats of silicates may be approximated from the specific heats of the constituent oxides. Their specific heats at elevated temperatures may be approximated by assuming an increase of 0.078 per cent per degree [$C_t = C_0(1 + 0.00078t)$].

Silicate slags, liquid: Acid slags, 0.30. Basic slags, 0.25.

The heat content (above 0°C.) of liquid silicate slags at their melting points varies from about 300 to 450 Cal. per kilogram, depending largely on the elevation of the melting point. For example, it is probably about 300 Cal. for a slag melting around 1100°C. and about 450 Cal. for one melting around 1400°C.

TABLE XX.—MEAN SPECIFIC HEAT OF SILICA[1]
(Between 0 and t°C.) (In kilogram-calories per kilogram, gram-calories per gram, or pound-calories per pound)

Temperature, °C.	c_m, quartz	c_m, cristobalite[2]	c_m, vitreous
0	0 166	0 170	0 165
50	0.177	0.179	0.176
100	0 186	0.190	0 185
200	0 202	0.212	0 200
300	0 216	0 231	0 212
400	0 228	0 237	0.222
500	0 238	0.243	0 231
600	0 252	0 248	0 238
700	0.255	0.253	0 244
800	0.257	0.257	0.249
900	0.259	0.261	0 253
1000	0.262	0.264	0 257
1100	0 264	0 267	0 260
1200	0 265	0 269	0 263
1300	0 267	0.271	0 267
1400	0 269	0 273	0 270
1500		0 275	0.275
1600		0.277	0 279
1700		0.279	0 283

[1] SOSMAN, R. B., "International Critical Tables," Vol V, 1929
[2] Made at 1100°C

TABLE XXI.—MEAN SPECIFIC HEATS OF REFRACTORIES[1]
(In gram-calories per gram, kilogram-calories per kilogram, or pound-calories per pound)

Refractory	c_m, 25–100°C.	c_m, 25–500°C.	c_m, 25–1000°C.	c_m, 25–1500°C.
Alumina, Al_2O_3	0.200	0.239	0.261	0.275
Alundum	0.186			
Carbon........	0.123	.....	0.31	
Chrome brick .	0.170	0.20	0 22	
Fire-clay brick.	0.20 ±0.01	0.22 ±0 01	0.26 ±0.01	0.30 ±0.01
Graphite........	....	....	0.294	0 410
Magnesia, MgO. .	0 235±0.005	0.26 ±0.005	0.28 ±0.005	0.29 ±0.005
Magnesite brick. .	0.22 ±0.01	0.25 ±0.01	0.28 ±0.01	0.30 ±0.01
Silica brick......	0 20 ±0.015	0.225±0.015	0.265±0.015	0.295±0 015
Silicon-carbide brick..........	0 200±0.031	....	0.187±0.041	
Zirconia, ZrO.	0 110±0 005	0.13	0 16	0 18

[1] "International Critical Tables," Vol. II, p. 85, 1927.

TABLE XXII.—VAPOR-PRESSURE CONSTANTS OF THE ELEMENTS[1]

The columns headed A, B, A', and B' give the values of the constants in the equations $\log p = -\frac{A}{T} + B$ for the vapor pressure p (in millimeters of mercury) for the liquid elements and $\log p = -\frac{A'}{T} + B'$ for the solid elements. $A = \frac{\Lambda}{4.578}$, where Λ is the energy change expressed in calories. T is the temperature in degrees centigrade on the absolute scale (C.° + 273). For further explanation see page 349. (Where no temperature range is stated, the figures given have been calculated from data in Table XII.)

Element	Symbol	Liquid state			Solid state		
		Temperature range covered, °C.	A	B	Temperature range covered, °C	A'	B'
Aluminum	Al		13,310	8.59		13,870	9.29
Antimony	Sb	1070–1325	10,180	8.824		11,220	9.976
Arsenic	As	. .			440– 815	6,950	10.800
Barium	Ba	930–1130	7,800	6.982	..	8,310	7.498
Bismuth	Bi	1210–1420	10,450	8.876	....	11,000	9.877
Cadmium	Cd	500– 840	5,200*	7.887*	150– 321	5,690	8.564
Calcium	Ca	960–1110	8,000	7.446	500– 700	8,490	7.880
Carbon	C	3880–4430	28,200	9.596			
Chromium	Cr		16,700	8.95		17,600	9.44
Cobalt	Co	2375	16,100	7.571		16,900	7.950
Copper	Cu	2100–2310	15,970	8.449		16,770	9.039
Gold	Au	2315–2500	17,880	8.400		18,540	8.897
Iron	Fe	2220–2450	18,480	8.527		19,270	8.965
Lead	Pb	525–1325	9,190	7.445		9,460	7.899
Magnesium	Mg	900–1070	7,120	8.029		7,590	8.538
Manganese	Mn	1510–1900	12,000	7.83		12,800	8.37
Mercury	Hg	400–1300	3,066	7.752	(−80)–(−39)	3,810	10.383
Molybdenum	Mo		28,100	8.42	1800–2240	29,600	8.92
Nickel	Ni	2360	19,100	9.242		20,020	9.774
Palladium	Pd	.	15,600	6.71		16,500	7.20
Phosphorus	P	44–635	5,667†	11.084†	20– 44	3,297	9.651
Platinum	Pt		23,370	7.881	1425–1765	24,400	8.385
Potassium	K	260– 760	4,430	7.183	..	4,556	7.558
Selenium	Se	700–1000	5,570	8.726		6,100	9.808
Silicon	Si		8,660	6.26	1200–1320	8,900	5.950
Silver	Ag	1650–1950	13,270	8.225	..	13,860	8.704
Sodium	Na	180– 883	5,395	7.553		5,532	7.922
Strontium	Sr	940–1140	7,350	7.328		7,830	7.794
Sulphur	S	445– 700	3,745	8.10		3,807	8.26
Tellurium	Te		11,700	11.46		13,100	13.40
Tin	Sn	1950–2270	14,800	8.701		16,300	11.672
Titanium	Ti		1,525	3.35		2,472	3.81
Tungsten	W		38,600	9.13	2230–2770	40,400	9.62
Zinc	Zn	600– 985	6,163‡	8.108‡	250– 419	6,950§	9.200§

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[1] Largely from "International Critical Tables," Vol. III, 1928, with revisions.

* Given more accurately by the equation $\log p = -\frac{5,800}{T} - 1.203 \log T + 12.107$.

† Given more accurately by the equation $\log p = -\frac{2,898}{T} - 1.257 \log T + 11.569$

‡ Given more accurately by the equation $\log p = -\frac{6,789.5}{T} - 1.051 \log T - 0.0001255T + 12.0181$ (temperature range, 419.5 to 1500°)

§ Given more accurately by the equation $\log p = -\frac{6,939.0}{T} - 0.1458 \log T - 0.0002883T + 9.7756$ (temperature range, 0 to 419.5°).

TABLE XXIII.—VAPOR-PRESSURE CONSTANTS, MELTING POINTS, AND BOILING POINTS OF COMPOUNDS[1]

A and *B* for the liquid state; see preceding table for explanation

Compound	Melting point, degrees centigrade	Normal boiling point, degrees centigrade	Temperature range covered, degrees centigrade	*A*	*B*
AgCl	455	1560	1255–1442	9,690	8 179
Al_2O_3	2045	2980	1840–2200	28,200	11 55
As_4O_6	313	457	315–490	6,656	11 988
CH_4O	−97	65	−10–80	2,002	8 955
CuCl	430	1490	878–1369	4,220	5 275
$HgCl_2$	282	305	275–309	3,190	8 409
KCl	770	1407	906–1105	9,120	8 353
KCl			1116–1418	8,870	8 130
KOH		1322	1170–1327	7,110	7.330
NaCl	800	1465	976–1155	9,420	8.330
NaCl			1156–1430	9,720	8 548
NaCN	622	1496	800–1360	8,120	7 472
NaF	992	1700	1562–1701	11,400	8.640
NaOH	322	1374	1010–1402	6,900	7 030
$Ni(CO)_4$	−25	43	2–40	1,566	7.780
$PbCl_2$	498	954	500–950	7,420	8 961
$SbCl_3$	72	219	170–253	2,576	8 090
SiO_2	1470–1700	2230	1860–2230	26,400	13 43
A and *B* for the solid state (sublimation)					
$AlCl_3$	190 (2.5 atm.)	180	70–190	6,010	16 24
As_4O_6		356	100–310	5,816	12 127
$SnCl_4$	−33	113	(−52) − (−38)	2,441	9 824

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[1] Largely from "International Critical Tables," Vol. III, 1928

TABLE XXIV.—MAXIMUM VAPOR PRESSURE OF WATER[1]
(Or pressure of saturated steam)

Temperature, °C	Pressure, mm Hg	Pressure, lb per sq in.	Temperature, °F.	Temperature, °C.	Pressure, mm. Hg	Pressure, lb per sq in	Temperature, °F
−30	0.3	0.006	−22	29	30.0	0.58	84
−25	0.5	0.009	−13	30	31.8	0.61	86
−20	0.8	0.015	− 4	32	35.7	0.69	90
−15	1.2	0.024	+ 5	34	39.9	0.77	93
−10	2.0	0.038	14	36	44.6	0.86	97
− 5	3.0	0.058	23	38	49.7	0.96	100
− 2	3.9	0.076	28	40	55.3	1.07	104
0	4.6	0.089	32	45	71.9	1.39	113
+ 2	5.3	0.103	36	50	92.5	1.79	122
4	6.1	0.118	39	55	118.0	2.28	131
6	7.0	0.136	43	60	149.4	2.89	140
8	8.0	0.155	46	65	187.5	3.63	149
10	9.2	0.178	50	70	233.7	4.52	158
11	9.8	0.190	52	75	289	5.60	167
12	10.5	0.203	54	80	355	6.88	176
13	11.2	0.217	55	85	434	8.40	185
14	12.0	0.232	57	90	526	10.16	194
15	12.8	0.248	59	95	634	12.26	203
16	13.6	0.263	61	100	760	14.70	212
17	14.5	0.281	63	110	1,075	20.80	230
18	15.5	0.300	64	120	1,491	28.85	248
19	16.5	0.319	66	130	2,030	39.26	266
20	17.5	0.339	68	140	2,718	52.55	284
21	18.6	0.360	70	150	3,581	69.26	302
22	19.8	0.383	72	160	4,652	89.96	320
23	21.1	0.408	73	170	5,962	115.29	338
24	22.4	0.433	75	180	7,546	145.93	356
25	23.8	0.461	77	190	9,443	182.61	374
26	25.2	0.488	79	200	11,689	226.04	392
27	26.7	0.516	81	210	14,325	277.01	410
28	28.3	0.548	82	220	17,390	336.30	428

Below 0°C., pressures are those of ice.

TABLE XXV.—MAXIMUM VAPOR PRESSURE OF MERCURY[1]
(In millimeters of mercury)

°C.	p	°C.	p	°C.	p
−30	0.000005	120	0.746	270	123.5
−20	0.000018	130	1.186	280	156.9
−10	0.000061	140	1.845	290	197.6
0	0.000185	150	2.807	300	246.8
10	0.000490	160	4.189	310	305.9
20	0.001201	170	6.128	320	376.3
30	0.002777	180	8.796	330	459.7
40	0.006079	190	12.423	340	557.9
50	0.01267	200	17.287	350	672.7
60	0.02524	210	23.72	360	806.2
70	0.04825	220	32.13	370	960.7
80	0.08880	230	42.99	380	1,138.4
90	0.1582	240	56.85	390	1,341.9
100	0.2729	250	74.37	400	1,574.1
110	0.4572	260	96.30	*	*

[1] "International Critical Tables," Vol III, 1928.

* 400–1300°C.: $\log p = -\frac{3,066}{T} + 7.752$.

Heats of Formation.—Tables XXVI to XLIX give the number of calories liberated by the union of the substances separated by commas in the first column. The unit is the gram-calorie per gram-mol of substance in the second column and per gram of substance in the third column (or kilogram-calorie per kilogram, or pound-calorie per pound). The item (Na_3, As, O_4) in the first column followed by 366,000 in the second column is equivalent to writing:

$$3Na + As + 4O = Na_3AsO_4; \qquad \Delta H = -366,000$$

A minus sign in the table before the number of calories indicates that the heat is absorbed instead of liberated when the union takes place, *i.e.*, that ΔH is positive when the compound is formed.

To convert the values given to B.t.u. per pound, multiply by 1.8.

The figures in the columns headed "To dilute solution" are the values for the heat of formation when the end product is a dilute aqueous solution instead of the anhydrous substance. These values include the heat of solution of the substance in a relatively large amount of water as well as the heat of combination of the elements or compounds indicated. The heat of formation or the heat of a reaction will vary somewhat with the concentration of the solution, but the variation grows smaller as the solution becomes more dilute. The values given, therefore, cannot be taken as wholly fixed, but the designation "dilute solution" indicates that the amount of water is relatively large and sufficient to place the heat of solution in the range where it no longer changes rapidly with change of dilution. The amount of water associated varies for different compounds, but whenever possible is given for a dilution of 1,000 molecules of H_2O per molecule of solute or as near to that dilution as possible.

In writing reactions the presence of the water is sometimes shown by the symbol (*aq*). Thus we may write:

$$3Na + As + 4O = Na_3AsO_4\ (aq); \qquad \Delta H = -381{,}600 \text{ cal.}$$

With few exceptions the values given are derived from those tabulated by F. R. Bichowsky and F. D. Rossini,[1] based on a revision of values compiled by Bichowsky in the "International Critical Tables," Vol. V, 1929. The values of heats of formation and heats of reaction vary with the temperature at which the reaction takes place. It is stated by the above writers that all the values given have been either determined for or calculated to the base temperature of 18°C.; *i.e.*, the reacting substances and the products both are at 18°. It is often convenient to use the values as though they were for the temperature of 0°C., and for most purposes this can be done without introducing an error of any importance. To obtain the correct values for 0°C., we should subtract from the figure given the heat content of the reacting substances at 18° (*i.e.*, the difference between the heat content at 0° and at 18°) and add the heat content of the products at 18°. Obviously these two quantities offset each other and make the net change relatively small; in most cases it is likely to be smaller than the probable error in the values given. The calorie used by Bichowsky and Rossini is the defined calorie equal to 4.1850 absolute joules or 4.1833 international joules.

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[1] "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corporation, New York, 1936.

TABLE XXVI.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF ARSENATES

A. From the Elements

Formula	Anhydrous		To dilute solution	
	Per formula weight	Per unit weight of metal	Per formula weight	Per unit weight of metal
(H_3, As, O_3)			175,300	58,540
(H_3, As, O_4)	214,900	71,080	214,500	70,950
(Ca_3, As_2, O_8)	794,000	6,600		
(Na_3, As, O_4)	366,000	5,304	381,600	5,530

B. From the Oxides and As_2O_3 or As_2O_5

Formula	Per formula weight	Per unit weight of oxide	Per formula weight	Per unit weight of oxide
$(3H_2O, As_2O_3)$			6,500	120
$(3H_2O, As_2O_5)$	38,400	710	38,600	715
$(3CaO, As_2O_5)$	121,300	721		
$(3Na_2O, As_2O_5)$	215,700	1,160	245,900	1,322

TABLE XXVII.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF BORATES

Formula	Anhydrous		To dilute solution	
	Per formula weight	Per unit weight of metal	Per formula weight	Per unit weight of metal
(H_3, B, O_3)	252,000	23,300	246,000	22,800
(Na_2, B_4, O_7)	742,000	16,140	752,500	16,360

TABLE XXVIII.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF BROMIDES

Formula	Anhydrous		To dilute solution	
	Per formula weight	For unit weight of metal	Per formula weight	Per unit weight of metal
(Ag, Br)	23,800	221		
(Au, Br_3)	14,500	74	10,800	55
(H, Br), gas	8,660	8,600	28,600	23,380
(K, Br)	94,030	2,405	88,890	2,270
(Na, Br)	86,330	3,754	86,100	3,744

TABLE XXIX.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF CARBIDES

Formula	Anhydrous		To dilute solution	
	Per formula weight	Per unit weight of metal	Per formula weight	Per unit weight of metal
(Al_4, C_3)	60,000	556		
(Ca, C_2)	14,600	364		
(Cl_4, C), gas	25,400	179		
(Cl_4, C), liq	33,200	234		
(Cr_3, C_2)	140,000	898		
(Fe_3, C)	− 5,200	− 31		
(H_4, C)	18,240	4,520		
(Mn_3, C)	23,000	140		
(N_2, C_2), gas	−70,800	−2,530	−64,100	−2,290
(Na_2, C_2)	− 4,800	− 104		
(Ni, C_3)	− 9,200	− 157		
(S_2, C), gas	−22,000	− 343		
(S_2, C), liq	−15,400	− 240		
(Si, C)	28,000	1,000		
(Ti, C)	110,000	2,300		

TABLE XXX.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF CARBONATES AND BICARBONATES

A. From the Elements

Formula	Anhydrous		To dilute solution	
	Per formula weight	Per unit weight of metal	Per formula weight	Per unit weight of metal
(Ba, C, O_3)	290,900	2,117		
(Ca, C, O_3)	289,500	7,223		
(Cu, C, O_3)	135,500	2,130		
(Fe, C, O_3)	172,800	3,094		
(H_2, C, O_3)			167,500	83,100
(K_2, C, O_3)	275,000	3,517	281,400	3,599
(Mg, C, O_3)	267,800	11,000		
(Mn, C, O_3)	218,000	3,977		
(Na_2, C, O_3)	270,600	5,883	276,200	6,005
(Na, H, C, O_3)	226,400	9,843	222,300	9,665
(Pb, C, O_3)	168,800	814		
(Zn, C, O_3)	193,300	2,957		

TABLE XXX.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF CARBONATES AND BICARBONATES.—(*Concluded*)

B. From the Metal Oxides and CO_2

Formula	Per formula weight	Per unit weight of oxide	Per formula weight	Per unit weight of oxide
(BaO, CO_2)	63,500	414		
(CaO, CO_2)	43,450	775		
(CuO, CO_2)	6,200	78		
(FeO, CO_2)	14,050	196		
(H_2O), CO_2)			15,300	850
(K_2O, CO_2)	94,300	1,000	100,700	1,071
(MgO, CO_2)	27,800	690		
(MnO, CO_2)	27,050	382		
(Na_2O, CO_2)	76,400	1,230	82,000	1,320
(Na_2O, H_2O, $2CO_2$)	106,650	1,720	98,450	1,588
(PbO, CO_2)	21,900	98		
(ZnO, CO_2)	15,500	191		

C. Dolomite from the Carbonates

($MgCO_3$, $CaCO_3$)	2,200	55 (MgO)		

TABLE XXXI.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF CHLORATES, PERCHLORATES, AND HYPOCHLORITES

From the Elements

Formula	Anhydrous		To dilute solution	
	Per formula weight	Per unit weight of metal	Per formula weight	Per unit weight of metal
(H, Cl, O)			29,800	29,600
(H, Cl, O_3)			20,800	20,640
(H, Cl, O_4)	19,350	19,200	39,600	39,300
(K, Cl, O)			86,140	2,203
(K, Cl, O_3)	91,330	2,334	81,060	2,071
(K, Cl, O_4)	112,100	2,866	100,430	2,569
(Na, Cl, O)			83,500	3,630
(Na, Cl, O_3)	83,600	3,635	78,220	3,400
(Na, Cl, O_4)	101,130	4,404	97,300	4,230

TABLE XXXII.—HEATS EVOLVED $(-\Delta H)$ IN FORMATION OF CHLORIDES

A. From the Elements

Formula	Anhydrous		To dilute solution	
	Per formula weight	Per unit weight of metal	Per formula weight	Per unit weight of metal
(Ag, Cl)	30,600	284		
(Al, Cl_3)	166,700	6,180	244,700	9,070
(Au, Cl_3)	28,300	144	32,750	166
(Au, H, Cl_4)			76,700	389
(Ba, Cl_2)	205,300	1,495	207,500	1,511
(Be, Cl_2)	112,500	12,480	163,600	18,150
(Bi, Cl_3)	90,610	434		
(Bi, O, Cl)	89,800	429		
(C, Cl_4) gas	25,400	2,120		
(C, Cl_4) liq	33,200	2,770		
(Ca, Cl_2)	190,700	4,760	208,600	5,207
(Ca, O, Cl_2)	178,700	4,460	188,500	4,710
(Cd, Cl_2)	93,000	827	96,100	855
(Ce, Cl_3)	261,500	1,865	283,600	2,020
(Co, Cl_2)	77,000	1,305	95,390	1,618
(Cu, Cl)	34,300	540		
(Cu, Cl_2)	53,400	841	64,600	1,016
(Fe, Cl_2)	81,870	1,466	99,760	1,787
(Fe, Cl_3)	96,400	1,725	128,000	2,290
(H, Cl) gas	22,060	21,890	39,600	39,280
(Hg_2, Cl_2)	63,150	157		
(Hg, Cl_2)	53,430	266	50,200	251
(Ir, Cl_3)	20,500	107	40,700	211
(K, Cl)	104,300	2,668	99,860	2,554
(K_2, Pt, Cl_6)	300,000	1,536 (Pt)	286,500	1,467 (Pt)
(K_2, Pd, Cl_6)	292,000	2,735 (Pd)	277,000	2,596 (Pd)
(Li, Cl)	97,400	14,040	106,000	15,270
(Mg, Cl_2)	153,200	6,300	189,100	7,777
(Mn, Cl_2)	112,700	2,051	128,800	2,345
(N, H_4, Cl)	75,080	4,408 (NH_3)	71,260	4,184 (NH_3)
(Na, Cl)	98,360	4,277	97,085	4,222
(Ni, Cl_2)	74,980	1,278	94,270	1,606
(Pb, Cl_2)	85,660	413	79,120	382
(Pd, Cl_2)	44,200	414		
(Pd, Cl_2, N_2, H_6)	105,400	988		
(Pt, Cl_4)	62,600	321	82,000	420
(Pt, Cl_2, N_2, H_6)	119,600	613		
(Pt, Cl_4, N_2, H_8)	194,000	994	185,600	952
(Sb, Cl_3) solid	91,400	751		
(Sb, Cl_5) solid	107,400	882		
(Sn, Cl_2)	81,150	683		
(Sn, Cl_4) gas	118,300	1,000		
(Sn, Cl_4) liq	127,300	1,073		
(Sr, Cl_2)	197,800	2,258	209,100	2,387
(Th, Cl_4)	335,000	1,444	392,000	1,689
(Ti, Cl_4) liq	181,400	3,787		
(Zn, Cl_2)	99,550	1,523	115,300	1,763
(Zn, Cl_2, N_2, H_6)	165,600	2,533		

B. Combination of Chlorides

Formula	Per formula weight	Per unit weight of first chloride	Per unit weight of second chloride
$(KCl, MgCl_2)$	3,040	41	32
$(2KCl, MgCl_2)$	2,480	17	26
$(ZnCl_2, 2NH_3)$	44,200	324	1,300

TABLE XXXIII—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF CHROMATES AND BICHROMATES

A. From the Elements

Formula	Anhydrous		To dilute solution	
	Per formula weight	Per unit weight of metal	Per formula weight	Per unit weight of metal
(H_2, Cr, O_4)			210,200	104,300
(K_2, Cr, O_4)	333,400	4,263	328,100	4,196
(K_2, Cr_2, O_7)	488,500	6,247	471,300	6,027
(Na_2, Cr, O_4)	319,800	6,952	322,300	7,007
(Na_2, Cr_2, O_7)			465,600	10,122
(Pb, Cr, O_4)	221,400	1,069		

B. From the Oxides and CrO_3

Formula	Per formula weight	Per unit weight of oxide	Per formula weight	Per unit weight of oxide
(H_2O, CrO_3)			13,000	722
(K_2O, CrO_3)	107,200	1,138	102,000	1,084
(K_2O, $2CrO_3$)	123,400	1,310	106,500	1,131
(Na_2O, CrO_3)	80,800	1,303	83,200	1,341
(Na_2O, $2CrO_3$)			87,100	1,405
(PbO, CrO_3)	29,600	132		

TABLE XXXIV.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF CYANIDES, ETC. From the Elements

Formula	Anhydrous		To dilute solution	
	Per formula weight	Per unit weight of metal	Per formula weight	Per unit weight of metal
(Ag, C, N)	−33,400	−310		
(Ca, C, N_2)	85,100	2,120		
(Ca, C_2, N_2)			60,500	1,510
(Cu, C, N)			−20,900	−329
(H, C, N), gas	−30,100	−29,800	−23,900	−23,700
(H, C, N), liq.	−23,700	−23,500		
(K, C, N)	28,500	729	25,500	652
(K, C, N, S)	47,400	1,211	41,280	1,055
(K, Ag, C_2, N_2)	6,900	64 (Ag)	−1,400	−13 (Ag)
(K, Au, C_2, N_2)			4,800	24 (Au)
(N, H_4, C, N)	1,100	61	− 3,350	−186
(Na, C, N)	22,900	1,000	22,400	976
(Na, C, N, S)	40,360	1,755	38,490	1,673
(Na, Ag, C_2, N_2)			− 4,200	−39 (Ag)
(Zn, C_2, N_2)	−16,200	−250		

TABLE XXXV.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF FLUORIDES

Formula	Anhydrous		To dilute solution	
	Per formula weight	Per unit weight of metal	Per formula weight	Per unit weight of metal
(Al, F_3)	329,000	12,200	360,100	13,350
(Ba, F_2)	288,000	2,097	285,000	2,076
(Be, F_2)			240,800	26,700
(Ca, F_2)	290,200	7,240		
(H, F), gas	64,000	63,500	75,700	75,100
(H, F), liq.	71,000	70,400		
(K, F)	134,100	3,430	138,200	3,535
(Li, F)	145,500	20,970	144,500	20,820
(Mg, F_2)	264,000	10,840		
(Na, F)	136,300	5,927	135,700	5,901
(Na_3, Al, F_6)	758,470	28,120 (Al)	767,800	28,470 (Al)
(Pb, F_2)	159,400	769		
(Si, F_4), gas	360,100	12,840		
(Si, H_2, F_6)			545,000	19,420
(Sn, H_2, F_6)			470,000	3,960

TABLE XXXVI.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF HYDRATES

A. From the Elements

Formula	Anhydrous		To dilute solution	
	Per formula weight	Per unit weight of metal	Per formula weight	Per unit weight of metal
(Al, O_3, H_3)	304,700	11,300		
(Ba, O_2, H_2)	225,900	1,644	237,500	1,729
(Be, O_2, H_2)	206,700	22,910		
(Ca, O_2, H_2)	236,100	5,890	238,800	5,960
(Cd, O_2, H_2)	134,600	1,190		
(Co, O_2, H_2)	131,500	2,230		
(Fe, O_2, H_2)	135,900	2,433		
(Fe, O_3, H_3)	197,400	3,535		
(K, O, H)	102,000	2,609	114,800	2,937
(Li, O, H)	116,000	16,800	121,000	17,450
(Mg, O_2, H_2)	219,000	8,980		
(Mn, O_2, H_2)	163,400	2,970		
(Mn, O_3, H_3)	220,000	4,000		
(N, H_4, O, H)			87,670	5,147 (NH_3)
(Na, O, H)	101,900	2,212		
(Ni, O_2, H_2)	129,800	3,351		
(Ni, O_3, H_3)	163,200	2,781		
(Pb, O_2, H_2)	123,000	5,940		
(Zn, O_2, H_2)	153,500	2,348		

B From the Metallic Oxides and H_2O

Formula	Per formula weight	Per unit weight of oxide	Per formula weight	Per unit weight of oxide
(Al_2O_3, $3H_2O$)	46,400	455		
(BaO, H_2O)	35,100	229	46,700	305
(BeO, H_2O)	7,700	308		
(CaO, H_2O)	26,700	476	29,400	524
(CdO, H_2O)	11,600	90		
(CoO, H_2O)	16,200	216		
(FeO, H_2O)	14,000	195		
(Fe_2O_3, $3H_2O$)	29,700	232		
(K_2O, H_2O)	59,900	637	85,500	909
(Li_2O, H_2O)	32,200	1,077	42,200	1,414
(MgO, H_2O)	15,600	387		
(MnO, H_2O)	18,600	262		
(Mn_2O_3, $3H_2O$)	39,500	250		
(NH_3, H_2O)			18,870	1,108 (NH_3)
(Na_2O, H_2O)	46,160	744	66,360	1,070
(NiO, H_2O)	14,200	190		
(PbO, H_2O)	13,140	63		
(ZnO, H_2O)	12,300	146		

TABLE XXXVII.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF HYDRIDES AND HYDROCARBONS

Formula	Anhydrous		To dilute solution	
	Per formula weight	Per unit weight of element which combines with hydrogen	Per formula weight	Per unit weight of element which combines with hydrogen
(As, H_3)	−43,500	−580		
(C, H_4)	18,240	1,520		
(C_2, H_2)	−53,900	−2,246	−49,900	−2,080
(C_2, H_4)	−11,000	−458		
(C_2, H_6)	20,960	873		
(C_3, H_8)	26,300	731		
(C_6, H_6) gas	−20,300	−282		
(C_6, H_6) liq	−12,500	−174		
(C, H_4, O) gas	48,440	4,036 (C)	59,700	4,960 (C)
(C, H_4, O) liq.	57,450	4,788 (C)		
(C_2, H_6, O) gas	56,950	4,742 (C)	69,820	5,813 (C)
(C_2, H_6, O) liq.	67,140	5,590 (C)		
(N, H_3), gas	10,940	782	19,350	1,381
(N, H_3), liq.	16,070	1,146		
(P, H_3)	2,300	164		
(Pd_2, H)	8,860	42		
(Pd_{15}, H)	4,600	3		
(Pt, H)	19,100	98		
(Pt_{10}, H)	14,200	7		
(Pt_{15}, H)	17,000	6		
(Sb, H_3)	−35,100	−288		

TABLE XXXVIII.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF IODIDES

Formula	Anhydrous		To dilute solution	
	Per formula weight	Per unit weight of metal	Per formula weight	Per unit weight of metal
(Ag, I)	14,900	139		
(Cu, I)	17,800	280		
(Cu, I_2)	4,800	76	11,700	184
(H, I) gas	− 5,930	−5,890	13,300	13,200
(K, I)	78,730	2,014	73,650	1,884
(Na, I)	69,450	3,021	70,870	3,082

TABLE XXXIX.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF MANGANATES AND PERMANGANATES

From the Elements

Formula	Anhydrous		To dilute solution	
	Per formula weight	Per unit weight of metal	Per formula weight	Per unit weight of metal
(H, Mn, O_4)			123,300	122,300
(K, Mn, O_4)	192,900	4,933 (K)	182,500	4,561 (K)
(Na_2, Mn, O_4)	270,000	5,870 (Na)		

TABLE XL.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF NITRATES

A From the Elements

Formula	Anhydrous		To dilute solution	
	Per formula weight	Per unit weight of metal	Per formula weight	Per unit weight of metal
(Ag, N, O_3)	29,400	273	23,960	222
(Ca, N_2, O_6)	224,040	5,590	227,940	5,686
(Co, N_2, O_6)	102,800	1,744	114,700	1,946
(Cu, N_2, O_6)	73,100	1,150	83,400	1,311
(Fe, N_2, O_6)			118,800	2,130
(Fe, N_3, O_9)			156,300	2,800
(H, N, O_3) gas	34,400	34,100	49,120	48,740
(H, N, O_3) liq	41,660	41,340		
(K, N, O_3)	118,093	3,020	110,100	2,817
(N, H_4, N, O_3)	87,930	5,163 (NH_3)	81,480	4,784 (NH_3)
(Na, N, O_3)	111,720	4,857	107,300	4,668
(Pb, N_2, O_6)	106,890	516	99,280	479
(Zn, N_2, O_6)			134,700	2,060

Table XL.—Heats Evolved ($-\Delta H$) in Formation of Nitrates.—(*Concluded*)

B. From the Oxides and N_2O_5

Formula	Per formula weight	Per unit weight of oxide	Per formula weight	Per unit weight of oxide
(Ag_2O, N_2O_5)	46,100	214	34,820	161
(CaO, N_2O_5)	72,200	1,286	76,200	1,358
(CoO, N_2O_5)	45,400	606	57,300	765
(CuO, N_2O_5)	35,200	443	45,500	572
(FeO, N_2O_5)			54,800	762
(Fe_2O_3, $3N_2O_5$)			115,900	726
(H_2O, N_2O_5) gas	11,640	647	40,560	2,250
(H_2O, N_2O_5) liq.	15,160	842		
(K_2O, N_2O_5)	150,100	1,594	133,600	1,418
($2NH_3$, H_2O, N_2O_5)	94,940	2,788 (NH_3)	82,040	2,410 (NH_3)
(Na_2O, N_2O_5)	124,000	2,000	114,950	1,855
(PbO, N_2O_5)	55,030	265	47,000	210
(ZnO, N_2O_5)			50,100	616

Table XLI.—Heats Evolved ($-\Delta H$) in Formation of Nitrides

Formula	Anhydrous		To dilute solution	
	Per formula weight	Per unit weight of metal	Per formula weight	Per unit weight of metal
(Al, N)	80,000	2,970		
(C_2, N_2) gas	− 70,800	−2,950	−64,100	−2,670
(C_2, N_2) liq.	− 65,500	−2,730		
(Ca, N_6)	− 75,800	−1,890		
(Ca_3, N_2)	109,000	907		
(Fe_4, N)	− 1,100	− 20		
(H_3, N) gas	10,940	3,620	19,350	6,400
(H_3, N) liq	16,070	5,320		
(Mg_3, N_2)	116,000	1,590		
(Mn, N_6)	− 94,000	−1,711		
(Si_3, N_4)	157,000	1,855		

TABLE XLII.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF OXIDES

Formula	Anhydrous		To dilute solution	
	Per formula weight	Per unit weight of metal	Per formula weight	Per unit weight of metal
(Ag_2, O)	6,950	32		
(Al_2, O_3)	380,000	7,045		
(As_2, O_3)	154,000	1,026	149,000	992
(As_4, O_6) gas	250,000	836		
(As_2, O_5)	217,900	1,453	224,000	1,490
(Au_2, O_3)	−11,000	−28		
(B_2, O_3)	280,000	12,930	287,500	13,280
(Ba, O)	133,000	970		
(Ba, O_2)	151,600	1,104		
(Be, O)	135,000	14,970		
(Bi_2, O_3)	137,100	328		
(C, O)	26,840*	2,235*	29,600 (sat soln)	2,467
(C, O_2)	94,450*	7,873*	99,210 (sat. soln.)	8,261
(Ca, O)	151,600	3,790		
(Cd, O)	65,200	581		
(Ce, O_2)	233,400	1,666		
(Co, O)	57,600	978		
(Co_3, O_4)	196,500	1,111		
(Cr, O_3)	139,300	2,678	141,800	2,726
(Cr_2, O_3)	273,000	2,625		
(Cu, O)	38,500	606		
(Cu_2, O)	42,500	335		
(Fe, O)	64,300	1,151		
(Fe_3, O_4)	266,000	1,588		
(Fe_2, O_3)	198,500	1,777		
(H_2, O) gas	57,801	28.678		
(H_2, O) liq.	68,370	33,920		
(H_2, O_2) gas	33,590	16,665	45,660	22,650
(H_2, O_2) liq.	45,200	22,425		
(Hg, O)	21,700	108		
(Hg_2, O)	21,500	54		
(Ir, O_2)	50,000	259		
(K_2, O)	86,300	1,105		
(Li_2, O)	142,000	10,200		
(Mg, O)	146,100	6.007		
(Mn, O)	96,500	1,757		
(Mn_3, O_4)	345,000	2,094		
(Mn_2, O_3)	233,000	2,121		
(Mn, O_2)	123,000	2,239		
(Mo, O_2)	130,000	1,355		
(Mo, O_3)	176,500	1,840	178,000	1,855
(Mo, O_4)			163,000	1,700
(N_2, O) gas	−19,650	−701	−13,400	−478

TABLE XLII.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF OXIDES.—(*Concluded*)

Formula	Anhydrous		To dilute solution	
	Per formula weight	Per unit weight of metal	Per formula weight	Per unit weight of metal
(N, O)	−21,500	−1,540		
(N, O_2)	−8,030	−573		
(N_2, O_4) gas	−3,060	−109		
(N_2, O_5) gas	−600	−21		
(Na_2, O)	99,450	2,162		
(Na_2, O_2)	119,200	2,592		
(Ni, O)	57,800	985		
(O_2, O) (ozone)	−34,500		−32,700	
(Os, O_4) gas	80,000	419		
(Os, O_4) solid	93,500	490		
(P_2, O_5)	366,900	5,912		
(Pb, O)	52,500	253		
(Pb_3, O_4)	172,400	277		
(Pb, O_2)	65,000	314		
(Pd, O)	21,500	202		
(S, O_2) gas	70,940	2,212	79,150	2,470
(S, O_3) gas	93,900	2,930	139,000	4,340
(Sb_2, O_3)	165,800	672	128,300	527
(Sb_2, O_4)	213,000	874		
(Sb_2, O_5)	231,000	949	228,000	936
(Se, O_2)	56,360	714	55,500	701
(Si, O_2)	201,000	7,160		
(Sn, O_2)	138,000	1,163		
(Sr, O)	140,600	1,606		
(Ta_2, O_5)	499,000	1,379		
(Te, O_2)	77,580	608	76,500	600
(Th, O_2)	293,000	1,262		
(Ti, O_2)	218,000	4,551		
(Tl_2, O)	42,200	103		
(U_3, O_8)	845,200	1,183		
(U, O_3)	291,600	1,225		
(V_2, O_3)	330,000	3,238		
(V_2, O_5)	437,000	4,290		
(W, O_3)	195,700	1,064		
(Zn, O)	83,500	1,277		
(Zr, O_2)	258,100	2,829		

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* These values are for carbon in the form of diamond. Values for amorphous carbon, as in fuels, are considerably higher. We recommend use of the figures 29,160 and 97,200 for CO and CO_2, respectively, equivalent to 2,430 and 8,100 per unit weight of carbon, respectively.

TABLE XLIII.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF PHOSPHATES AND PHOSPHIDES

A. From the Elements

Formula	Anhydrous		To dilute solution	
	Per formula weight	Per unit weight of metal	Per formula weight	Per unit weight of metal
(Ca_3, P_2, O_8)	982,000	8,170	984,000	8,180
(Ca_4, P_2, O_9)	1,134,000	7,080		
(Ca, H, P, O_4)	433,000	10,800		
(Cu, P_2)	1,000	16		
(Fe, P)	0	0		
(H_3, P) gas	2,300	762		
(H_3, P, O_4) liq.	300,700	99,450	306,200	98,940
(K_3, P, O_4)			479,300	4,087
(K_2, H, P, O_4)			426,000	5,449
(K, H_2, P, O_4)	362,700	9,276	367,300	9,394
(Mg_3, P_2, O_8)	916,000	12,600		
(Mn_3, P)	70,900	430		
(Mn_2, P_3, O_{12})	736,000	6,700		
(Na, P, O_3)	289,000	12,560	293,000	12,730
(Na_3, P, O_4)	457,000	6,620	471,300	6,831
(Na_2, H, P, O_4)	415,000	9,023	420,600	9,145

B. From the Oxides and P_2O_5

Formula	Per formula weight	Per unit weight of oxide	Per formula weight	Per unit weight of oxide
$(3CaO, P_2O_5)$	160,300	953		
$(4CaO, P_2O_5)$	160,700	717		
$(2CaO, P_2O_5, H_2O)$	138,100	1,231		
$(3H_2O, P_2O_5)$	61,000	1,128	72,000	1,333
$(3K_2O, P_2O_5)$			332.800	1,177
$(2K_2O, P_2O_5, H_2O)$			254,700	1,351
$(K_2O, P_2O_5, 2H_2O)$	163,600	1,737	165,700	1,760
$(3MgO, P_2O_5)$	112,300	929		
$(3MnO, P_2O_5)$	105,100	495		
(Na_2O, P_2O_5)	111,300	1,795	119,300	1,924
$(3Na_2O, P_2O_5)$	255,600	1,374	282,600	1,519
$(2Na_2O, P_2O_5, H_2O)$	206,300	1,665	217,500	1,755

TABLE XLIV.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF SILICATES

A. From the Elements

Formula	Per formula weight	Per unit weight of metal	Per unit weight of SiO_2
(Al_2, Si, O_5)	617,000	11,440	10,270
(Al_2, Si_2, O_7)	800 000	13,750	6,660
(Al_6, Si_2, O_{13})	1,804,000	11,150	15,020
(Al_2, Si_2, O_8, H_2)	945,000	17,520	7,870
(Ca, Si, O_3)	377,900	9,429	6,290
(Ca, Si, O_4)	537,000	13,400	8,870
(Ca_3, Si, O_5)	684,400	5,690	11,400
(Fe, Si, O_3)*	273,500	4,900	4,515
(Fe_2, Si, O_4)	351,200	3,140	5,840
(Mg, Si, O_3)	346,500	14,250	5,780
(Mn, Si, O_3)	292,800	5,342	4,875
(Mn_3, Si_2, O_7)	679,000	3,190	5,650
(Na_2, Si, O_3)	371,200	8,070	6,180
(Zn, Si, O_3)	282,600	4,322	4,705
(Zn_2, Si, O_4)	340,400	2,603	5,668

B. From the Constituent Oxides

Formula	Per formula weight	Per unit weight of metal oxide	Per unit weight of SiO_2
(Al_2O_3, SiO_2)	36,000	353	600
$(Al_2O_3, 2SiO_2)$	8,500	84	71
$(3Al_2O_3, 2SiO_2)$	262,000	857	2,620
$(Al_2O_3, 2SiO_2, H_2O)$	95,700	939	797
(CaO, SiO_2)	25,200	449	420
(CaO_2, SiO_2)	179,600	3,200	2,990
$(3CaO, SiO_2)$	28,600	170	476
(FeO, SiO_2)*	8,200	114	136
$(2FeO, SiO_2)$	22,000	153	367
(MgO, SiO_2)	400	10	7
(MnO, SiO_2)	−4,700	−66	−78
$(3MnO, 2SiO_2)$	16,100	76	134
(Na_2O, SiO_2)	70,750	1,141	1,178
(ZnO, SiO_2)	−1,900	−23	−32
$(2ZnO, SiO_2)$ (vitreous)	−27,600	−170	−460

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* It has been shown that $FeSiO_3$ does not exist as a definite chemical compound, it is a solution of SiO_2 and Fe_2SiO_4.

TABLE XLV.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF SOME SODIUM SALTS

A. From the Elements

Formula	Anhydrous		To dilute solution	
	Per formula weight	Per unit weight of sodium	Per formula weight	Per unit weight of sodium
(Na, Al, O_2)	272,000	11,830		
(Na_2, Mo, O_4)	364,000	7,910	358,700	7,800
(Na, Pb, O_3)	202,400	8,800		
(Na_3, Sb, O_4)	349,000	5,060	360,000	5,220
(Na_4, Sn, O_4)	370,000	4,020	453,300	4,928
(Na_2, U, O_4)	500,000	10,870		
(Na_3, V, O_4)	449,000	6,510		
(Na_2, W, O_4)	391,000	8,500	381,300	8,290
(Na_2, Zn, O_2)	187,000	4,065		

B. From the Oxides

Formula	Per formula weight	Per unit weight of Na_2O	Per formula weight	Per unit weight of Na_2O
(Na_2O, Al_2O_3)	64,500	1,040		
(Na_2O, MoO_3)	88,000	1,420	82,750	1,332
(Na_2O_2, $2PbO_2$)	155,600	1,995 (Na_2O_2)		
($3Na_2O$, Sb_2O_5)	169,650	913	201,650	1,084
($2Na_2O$, SnO_2)	32,400	261	115,700	933
(Na_2O, UO_3)	108,950	1,755		
($3Na_2O$, V_2O_5)	161,600	870		
(Na_2O, WO_3)	95,850	1,545	86,150	1,388
(Na_2O, ZnO)	4,050	65		

TABLE XLVI.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF SULPHATES, ETC.

A. From the Elements

Formula	Anhydrous		To dilute solution	
	Per formula weight	Per unit weight of metal	Per formula weight	Per unit weight of metal
(Ag_2, S, O_4)	170,100	790	165,600	768
(Al_2, S_3, O_{12})	770,000	14,820	896,000	17,250
(Ba, S, O_4)	349,400	2,543	344,100	2,504
(Ca, S, O_4)	340,700	8,500	344,750	8,601
(Cd, S, O_4)	222,220	1,977	232,900	2,072
(Co, S, O_4)	216,700	3,677	231,700	3,931
(Cr_2, S_3, O_{12}) (violet)			771,400	7,416
(Cr_2, S_3, O_{12}) (green)			767,800	7,381
(Cu, S, O_4)	184,700	2,905	200,640	3,156
(Fe, S, O_4)	221,300	3,963	236,000	4,226
(Fe_2, S_3, O_{12})			653,200	5,850
(H_2, S, O_3)			146,700	72,500
(H_2, S, O_4)	193,750	96,130	212,400	105,400
(K_2, S, O_4)	342,660	4,382	336,170	4,299
(K, H, S, O_4)	276,850	7,080	273,800	7,002
(K, Al, S_2, O_8)	569,000	21,100 (Al)	617,500	22,900 (Al)
(Mg, S, O_4)	304,950	12,540	325,300	13,380
(Mn, S, O_4)	251,200	4,573	265,000	4,824
(N_2, H_8, S, O_4)	281,460	8,262 (NH_3)	279,000	8,190 (NH_3)
(Na_2, S, O_3)	261,200	5,678	263,900	5,737
(Na_2, S, O_4)	330,480	7,184	330,630	7,188
(Na, H, S, O_4)	269,040	11,697	270,800	11,770
(Na_2, S_2, O_3)	258,500	5,620	260,500	5,663
(Ni, S, O_4)	216,000	3,680	231,100	3,938
(Pb, S, O_4)	218,500	1,054		
(Zn, S, O_4)	233,400	3,572	251,950	3,855

B. From Metallic Oxides and SO_3

Formula	Per formula weight	Per unit weight of oxide	Per formula weight	Per unit weight of oxide
(Ag_2O, SO_3)	69,250	299	64,750	279
$(Al_2O_3, 3SO_3)$	108,300	1,060	234,300	2,300
(BaO, SO_3)	122,100	797	116,800	762
(CaO, SO_3)	95,100	1,696	99,150	1,768
(CdO, SO_3)	63,100	492	73,800	575
(CoO, SO_3)	65,300	872	80,300	1,070
$(Cr_2O_3, 3SO_3)$ (violet)			216,700	1,424
$(Cr_2O_3, 3SO_3)$ (green)			213,100	1,402
(CuO, SO_3)	52,300	657	68,240	858
(FeO, SO_3)	63,100	878	77,800	1,081
$(Fe_2O_3, 3SO_3)$			173,000	1,083
(H_2O, SO_2)			17,960	997
(H_2O, SO_3)	42,050	2,334	60,700	3,370
(K_2O, SO_3)	162,560	1,722	156,100	1,657
$(K_2O, 2SO_3, H_2O)$	221,900	2,356	215,400	2,290
$(K_2O, Al_2O_3, 4SO_3)$	296,200	2,909 (Al_2O_3)	393,200	3,863 (Al_2O_3)
(MgO, SO_3)	64,950	1,610	85,300	2,113
(MnO, SO_3)	60,800	858	74,600	1,050
$(2NH_3, H_2O, SO_3)$	107,760	3,163 (NH_3)	105,300	3,091 (NH_3)
(Na_2O, SO_2)	90,830	1,465	93,530	1,509
(Na_2O, SO_3)	137,130	2,212	137,280	2,214
$(Na_2O, 2SO_3, H_2O)$	193,030	3,113	196,550	3,170
(Na_2S, SO_3)	74,800	958 (Na_2S)	76,800	984 (Na_2S)
(NiO, SO_3)	63,700	853	78,800	1,054
(PbO, SO_3)	72,140	323		
(ZnO, SO_3)	56,000	689	105,600	1,300

TABLE XLVII.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF SULPHIDES

Formula	Anhydrous		To dilute solution	
	Per formula weight	Per unit weight of metal	Per formula weight	Per unit weight of metal
(Ag_2, S)	5,500	26		
(Al_2, S_3)	140,500	2,705		
(As_2, S_3)	20,000	133		
(Ba, S)	111,000	809	118,500	862
(C, S_2) gas	−22,000	−1,830		
(C, S_2) liq.	−15,400	−1,282		
(Ca, S)	113,500	2,835	119,700	2,990
(Cd, S)	34,700	309		
(Co, S)	22,300	379		
(Co_2, S_3)	39,900	339		
(Cu, S)	11,600	183		
(Cu_2, S)	18,950	149		
(Fe, S)	23,100	414		
(Fe, S_2)	35,500	636		
(H_2, S)	5,300	2,650	9,900	4,910
(Hg, S)	10,870	54		
(K_2, S)	121,500	1,554	110,600	1,415
(Mg, S)	82,200	3,380	108,000	4,440
(Mn, S)	47,400	862		
(Na_2, S)	89,900	1,955	105,200	2,288
(Ni, S)	20,800	355		
(Pb, S)	22,200	107		
(Sb_2, S_3)	36,000	148		
(Sn, S)	22,700	191		
(Zn, S)	44,000	674		

TABLE XLVIII.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF MOLECULAR FROM ATOMIC GASES

Formula	Per formula weight	Per unit weight of element	Per liter of gas formed, gram-calories
(H, H)	102,900	51,050	4,590
(O, O)	117,400	3,670	5,240
(N, N)	169,300	6,040	7,550
(Cl, Cl)	56,900	802	2,540

TABLE XLIX.—HEATS EVOLVED ($-\Delta H$) IN FORMATION OF MISCELLANEOUS COMPOUNDS

Formula	Per formula weight	Per unit weight of first element	Per unit weight of second element
(Au, Hg_{100})	−2,000	−10	0
(Cd, Hg_{55})	500	5	0
(Cd, $Zn_{0.36}$)	−3,600	−32	−153
(Cd, $Zn_{1.28}$)	-6,900	−61	−82
(Cd, $Zn_{4.61}$)	−6,000	−53	−20
(Cu, Al_2)	84,000	1,320	1,555
(Cu_3, Sb)	2,400	13	20
(Cu, Se)	19,000	299	241
(Cu_2, Se)	14,500	114	184
(Cu_3, Sn)	7,900	41	67
(Cu_2, Te)	6,000	47	47
(Cu_2, Zn_3)	16,000	126	82
(Fe, Al_5)	25,100	449	186
(Fe_3, Si)	−20,000	−119	−713
(Mg_4, Al_3)	49,000	504	606
(Mg, Zn_2)	13,150	541	104
(Na, Hg_2)	18,500	805	46
(Na, $Hg_{27.5}$)	19,600	852	4
(Na, Hg_{400})	20,070	872	0
(Pb, Hg_{100})	−2,500	−12	0
(Sn, Bi)	370	3	2
(Sn, Bi_2)	−170	−2	−1
(Sn_2, Bi)	−120	−1	−1
(Sn, Hg_{50})	−2,540	−21	0
(Zn, Hg_{65})	−2,300	−37	0
(Zn, Sn_2)	−6,000	−92	−25
(Zn, $Sn_{0.1}$)	−5,000	−77	−422

TABLE L.—NET HEATS OF COMBUSTION (LOW CALORIFIC POWERS) OF GASEOUS AND LIQUID FUELS[1]

(Water vapor formed in combustion not condensed)[1]

A. Gases

Formula	Name	Kilogram-calories per cubic meter[2]	B.t.u. per cubic foot[2]
H_2	Hydrogen	2,582	290
H_2S	Hydrogen sulphide	5,514	620
CO	Carbon monoxide	3,034	341
NH_3	Ammonia	3,385	380
CH_4	Methane	8,560	962
C_2H_2	Acetylene	13,440	1,510
C_2H_4	Ethylene	14,480	1,627
C_2H_6	Ethane	15,110	1,698
C_3H_4	Allylene (propyne)	19,420	2,182
C_3H_6	Propylene	20,670	2,322
C_3H_8	Propane	21,650	2,433
C_4H_8	Butylene	27,060	3,041
C_4H_{10}	Butane (isobutane)	28,220	3,171
C_6H_6	Benzene (benzol)	33,490	3,763

B. Liquids

Formula	Name	Kilogram-calories per kilogram	B.t.u. per pound
C_6H_6	Benzene (benzol)	9,632	17,340
C_7H_8	Toluene (toluol)	9,708	17,470
CH_4O	Methyl alcohol	4,676	8,417
C_2H_6O	Ethyl alcohol	6,435	11,580
C_3H_6O	Acetone	6,810	12,260
CS_2	Carbon bisulphide	2,880	5,185

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[1] To obtain the gross or high calorific power (water vapor condensed), add the following
For gases, 471 Cal. per cubic meter or 53 B.t.u. per cubic foot for each mol of H_2 in the gas.
For liquids, 10,560 Cal. per kilogram-molecular weight or 19,000 B.t.u. per pound-molecular weight for each mol of H_2 in the liquid.

[2] Volumes measured at standard conditions (0°C., 760 mm., or 32°F., 29.92 in.).

TABLE LI.—THERMAL RESISTIVITY OF VARIOUS MATERIALS[1]

(Most of the values must be regarded as typical, subject to variation in different samples)

Material	Density in bulk, grams per cubic centimeter	Resistivity, thermal ohms[2] per centimeter cube[3]	Resistivity, °F. per B t.u. per square foot per inch thickness per second	Temperature at which determined,[4] °C.
Air	0.00129	4,340	22,600	0
Alundum	....	30	150	650–1250
Asbestos, air-cel	0.14	1,380	7,200	25
Asbestos paper	0.8–1.1	550	2,900	65
Asbestos wool	0.40	1,100–1,000	5,700–5,200	0–100
Bauxite brick	2.53	220–150	1,150–780	100–1000
Brick, common red	1.75	200	1,040	20
Carbon	1.5	2.6–1.7	13.5–8.8	360–1500
Carborundum	2.0	17	88	1135
Carborundum brick	....	12.5–10	65–52	1000
Charcoal	0.18	1,820	9,500	20
Chrome brick	2.8	42	220	1000
Concrete	2.1	110	570	0
Copper	8.9	0.26	1.35	100
Cork	0.05–0.35	3,000–1,550	15,600–8,060	20
Diatomite	0.20–0.50	1,600–970	8,300–5,000	100
Felt, wool	0.33	1,920	10,000	30
Fire-clay brick	1.8–2.8	200–60	1,040–310	100–1500
Glass	2.6	140–130	730–680	20–100
Graphite, solid	1.8	0.70–0.87	3.65–4.53	400–1500
Gypsum, plaster	0.74	300	1,560	30
Iron, sheet	7.3	1.65–1.66	8.6–8.65	18–100
Magnesia, 85 %	0.3	1,330	6,900	30
Magnesite brick	2.5	41–21	210–110	100–1200
Manganin	....	1.57–2.64	8.2–13.7	18–100
Mercury (liquid)	13.6	16.2–12.7	84.3–66.1	0–50
Mica	....	170–240	880–1,250	50
Platinum	21.1	1.44–1.38	7.5–7.2	18–100
Porcelain	...	96	500	90
Sandstone	2.25	77	400	20
Sawdust	0.20	1,670	8,700	30
Silica, fused	2.20	100–94	520–490	20–100
Silica brick	1.6	140–75	730–390	100–1000
Sil-O-Cel brick	0.5	930	4,840	870
Sil-O-Cel powder	0.2–0.25	2,300	12,000	25
Slag wool	0.15–0.30	2,400–1,900	12,500–10,000	30
Slate, ⊥ cleavage	.	65–77	340–400	95
Slate, ‖ cleavage		37–44	190–230	95
Steel	7.2	2.2	11.4	18–100
Vacuum	0	17,000	88,000	150
Water	1.0	167	870	20
Wood, white pine, ⊥ grain	0.45	930	4,840	60
Wood, white pine, ‖ grain	0.45	390	2,030	60
Wool	0.09	2,700–2,000	14,000–10,500	0–60

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[1] Reciprocal of the thermal conductivity. Largely from "International Critical Tables," Vol. V, 1929.

[2] One thermal ohm = 1°C. per watt = 1°C. per joule per second (see p. 315).

[3] To convert from the unit per centimeter cube to the unit per inch cube, divide the value given by 2.54.

[4] The thermal resistance of most solids decreases with rise of temperature; that of most metals and alloys increases.

TABLE LII.—TOTAL EMISSIVITIES OF VARIOUS SURFACES[1]

Material	*E* at 50°C.	*E* at 300°C.	*E* at 500°C.	*E* at other temperatures
Black body, theoretical	1 00	1 00	1 00	1 00
Alumina			0 10	
Aluminum, highly polished			0.055	0 039 (230°)
Aluminum, oxidized		0 11 (200°)	0 15 (400°)	0 19 (600°)
Aluminum paint	0 27–0 67	....		0 45 (127°)
Asbestos	0 93	0.95		
Black paint, smooth	0 68			
Black [illegible]	0 64			
Brass polished	0 04	0 035		
Brass oxidized		0 61 (200°)	0 60 (400°)	0 59 (600°)
Cast iron, liquid		...		0 28 (1200–1750°)
Cast iron, new		0 21 (200°)		
Cast iron, polished	0 17			
Cast iron, oxidized	0 56	0 67	0 71 (400°)	0 78 (600°)
Chromite	0 99		....	0 99 (1000°)
Chromium	0 11		0 19	0 37 (1000°)
Copper, liquid				0 16 (1075°) 0 15 (1300°)
Copper, calorized	0 39	0 26	0 23	0 20 (1000°)
Copper, oxidized	0 77	0 70	0 73	0 70 (1000°)
Copper, polished	0 03			0 09 (1000°)
Cuprous oxide	0 60			0 61 (1170°)
Fire clay, white		0 73	0 79 (400°)	
Glass	0 49			
Gold, enamel	0 33			0 37 (126°)
Gold, polished	0.03		0 07	
Graphite, mat	0 90	0 82	0 92 (400°)	
Graphite polished	0 65	..	0 95	
Hematite			0.98	
Iron, galvanized, bright	0.23			
Iron, galvanized, gray oxidized	0 28			
Iron, sheet	0 47			
Iron, Russian sheet	0 56			
Iron-oxide scale			0 85	0 89 (1200°)
Iron rust				0 91 (440°) 0 85 (470°)
Lampblack	0 95–0 98			
Lead, oxidized	..	0 63 (200°)		
Lime	0 10		0 40	
Magnesia	0 06	.....	0 09	
Magnesium	0 07	0 14	0 23	
Molybdenum, filament		..		0 096 (725°) 0 292 (2600°)
Monel metal, bright	0 05			
Monel metal, oxidized	0 50	0 41	0 38	0 46 (600°)
Nickel, bright	0 045	0 087		0 17 (1000°)
Nickel, oxidized	0 35	0 40	0 48	0 88 (1300°)
Plaster	0 60			
Platinum, polished	0 035	0 061	0 08	0 124 (1000°) 0 175 (1700°)
Porcelain	0 25		0 50	
Silicon	0 72	..		0 72 (1000°)
Silver, polished	0.02	0 03	0.04	0 038 (600°)
Silvered paper	0 07			
Steel, liquid				0 28 (1600°)
Steel, calorized		0 52 (200°)	0 55 (400°)	0 57 (600°)
Steel, oxidized		0 79 (200°)	0 79 (400°)	0 79 (600°)
Steel, stainless, rough		0 44 (200°)	0 36	
Stone, building	0 60			
Tin, bright	0 04			
Tin plate	0 04			
Tungsten, aged filament	0.032			0 39 (3250°)
Wood	0 60			
Zinc, bright	0 04			
Zinc, oxidized			0 11 (400°)	
Zirconia	0 06		0.09	

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[1] From RICHARDS, JOSEPH W., "Metallurgical Calculations," McGraw-Hill Book Company, Inc , New York, 1918, with additions Most of the values must be regarded merely as typical, subject to variation with small changes in character of [illegible] from H. C. Hottel in Herman J. Stoever's "Applied Heat Transmission," [illegible] Inc , New York, 1941

TABLE LIII.—ELECTRICAL CONDUCTIVITIES AND SPECIFIC GRAVITIES OF SOLUTIONS[1]
(Conductivities in reciprocal ohms per centimeter cube, for aqueous solutions at 18°C.)

Salt	Per cent[2]	Normality[3]	Specific gravity, 18°C.	Conductivity	Temperature coefficient[4]
$AgNO_3$	5	0.307	1.042	0.0256	0.0218
	10	0.641	1.089	0.0476	0.0217
	15	1.006	1.140	0.0683	0.0215
	20	1.407	1.196	0.0872	0.0212
	25	1.847	1.256	0.1058	0.0210
	30	2.332	1.321	0.1239	0.0209
	35	2.872	1.394	0.1406	0.0207
$CuSO_4$	2.5	0.321	1.025	0.0109	0.0213
	5.0	0.658	1.051	0.0189	0.0216
	10.0	1.387	1.107	0.0320	0.0218
	15.0	2.194	1.167	0.0421	0.0231
	17.5	2.631	1.200	0.0458	0.0236
$FeSO_4$	3.68	0.50	1.034	0.0154	0.0218
	7.11	1.00	1.069	0.0258	0.0218
	13.36	2.00	1.137	0.0390	0.0223
	18.95	3.00	1.202	0.0461	0.0231
	21.86	3.56	1.236	0.0470	0.0243
H_2SO_4·	5	1.053	1.033	0.2085	0.0121
	10	2.176	1.067	0.3915	0.0128
	15	3.376	1.104	0.5432	0.0136
	20	4.655	1.141	0.6527	0.0145
	25	6.019	1.181	0.7171	0.0154
	30	7.468	1.221	0.7388	0.0162
	35	9.011	1.262	0.7243	0.0170
	40	10.649	1.306	0.6800	0.0178
	45	12.396	1.351	0.6164	0.0186
	50	14.258	1.398	0.5405	0.0193
KCl	5	0.691	1.031	0.0690	0.0201
	10	1.427	1.064	0.1359	0.0188
	15	2.208	1.098	0.2020	0.0179
	20	3.039	1.133	0.2677	0.0168
KCN	3.25	0.506	1.015	0.0527	0.0207
	6.50	1.029	1.032	0.1026	0.0193

TABLE LIII.—ELECTRICAL CONDUCTIVITIES AND SPECIFIC GRAVITIES OF SOLUTIONS.[1]—(*Concluded*)

Salt	Per cent[2]	Normality[3]	Specific gravity, 18°C.	Conductivity	Temperature coefficient[4]
NaCl	5	0.884	1.034	0.0672	0.0217
	10	1.830	1.071	0.1211	0.0214
	15	2.843	1.109	0.1642	0.0212
	20	3.924	1.148	0.1957	0.0216
	25	5.085	1.190	0.2135	0.0227
Na_2CO_3	5	0.991	1.051	0.0451	0.0252
	10	2.082	1.104	0.0705	0.0271
	15	3.277	1.159	0.0836	0.0294
NaOH	2.5	0.641	1.028	0.1087	0.0194
	5	1.319	1.057	0.1969	0.0201
	10	2.779	1.113	0.3124	0.0217
	15	4.381	1.170	0.3463	0.0249
	20	6.122	1.226	0.3270	0.0299
	25	8.002	1.282	0.2717	0.0368
	30	10.015	1.337	0.2022	0.0450
$NiSO_4$	3.72	0.5	1.038	0.0153	0.0231
	7.19	1.0	1.076	0.0254	0.0227
	13.46	2.0	1.150	0.0385	0.0241
	18.47	3.0	1.222	0.0452	0.0250
$ZnSO_4$	5	0.651	1.051	0.0191	0.0225
	10	1.371	1.107	0.0321	0.0223
	15	2.169	1.167	0.0415	0.0228
	20	3.053	1.232	0.0468	0.0241
	25	4.040	1.304	0.0480	0.0258
	30	5.124	1.379	0.0444	0.0273

[1] From LANDOLT and BÖRNSTEIN, "Physikalisch-chemische Tabellen," Julius Springer, Berlin, 1923, 1927, 1931. Determinations mostly by Kohlrausch, $FeSO_4$ and $NiSO_4$ by Klein

[2] Grams of salt or compound per 100 g. of solution.

[3] Gram equivalents per liter.

[4] The conductivity at 18° increases by this fraction of itself for every rise of 1° above 18 (mostly determined only to 26°).

TABLE LIV.—UNIT CONVERSION TABLES

A. Length, or Linear Measure

1 millimeter = 0.03937 inch
1 centimeter = 0.3937 inch
1 decimeter = 3.937 inches
1 decimeter = 0.3281 foot
1 meter = 39.370 inches
1 meter = 3.281 feet
1 meter = 1.0936 yards
1 kilometer = 3,281 feet
1 kilometer = 0.6214 mile
1 inch = 25.40 millimeters
1 inch = 2.540 centimeters
1 inch = 0.2540 decimeter
1 foot = 3.048 decimeters
1 inch = 0.0254 meter
1 foot = 0.3048 meter
1 yard = 0.9144 meter
1 foot = 0.000305 kilometer
1 mile = 5,280 feet = 1.609 kilometers

B. Area, or Square Measure

1 square millimeter = 0.00155 square inch
1 square centimeter = 0.1550 square inch
1 square decimeter = 15.50 square inches
1 square decimeter = 0.1076 square foot
1 square meter = 10.764 square feet
1 square meter = 1.1960 square yards
1 square meter = 0.000247 acre
1 hectare = 2.471 acres
1 square kilometer = 247.1 acres = 0.3861 square mile
1 square inch = 645.2 square millimeters
1 square inch = 6.452 square centimeters
1 square inch = 0.0645 square decimeter
1 square foot = 9.290 square decimeters
1 square foot = 0.0929 square meter
1 square yard = 0.8361 square meter
1 acre = 4,840 square yards = 4,047 square meters
1 acre = 0.4047 hectare
1 square mile = 640 acres = 2.590 square kilometers

C. Volume, or Cubic Measure

1 cubic centimeter = 0.0610 cubic inch
1 cubic centimeter = 0.03381 fluid ounce
1 liter = 61.03 cubic inches
1 liter = 2.1134 pints
1 liter = 1.0567 quarts (liq.)
1 liter = 0.2642 gallon (U. S.)
1 gallon (British) = 1.201 gallons (U. S.)
1 liter = 0.9081 quart (dry)
1 liter = 0.1135 peck (U. S.)
1 hectoliter = 2.8377 bushels (U. S.)

TABLE LIV.—UNIT CONVERSION TABLES.—(*Continued*)

1 cubic meter = 35.314 cubic feet
1 cubic meter = 1.3079 cubic yards
1 cubic inch = 16.387 cubic centimeters
1 fluid ounce = 29.57 cubic centimeters
1 cubic inch = 0.01639 liter
1 pint = 28.88 cubic inches = 0.47318 liter
1 quart (liq.) = 57.75 cubic inches = 0.94635 liter
1 gallon (U. S.) = 3.7854 liters
1 gallon (U. S.) = 0.8237 gallon (British)
1 quart (dry) = 67.21 cubic inches = 1.1012 liters
1 peck (U. S.) = 8.8098 liters
1 bushel (U. S.) = 0.3524 hectoliter
1 cubic foot = 0.02832 cubic meter
1 cubic yard = 0.7646 cubic meter

D. Weight

1 gram = 15.432 grains
1 gram = 0.03527 ounce (avoir.)
1 gram = 0.03215 ounce (troy)
1 gram = 0.00220 pound (avoir.)
1 kilogram = 2.20462 pounds (avoir.)
1 kilogram = 2.67923 pounds (troy)
1 metric ton = 2,204.6 pounds (avoir.)
1 metric ton = 1.1023 short tons
1 metric ton = 0.9842 long ton
1 grain = 0.06480 gram = 0.000143 pound
1 ounce (avoir.) = 28.35 grams
1 ounce (troy) = 31.10 grams
1 pound (avoir.) = 14.583 ounces (troy) = 453.59 grams
1 pound (avoir.) = 7,000 grains = 0.4536 kilogram
1 pound (troy) = 0.3732 kilogram
1 pound (avoir.) = 0.0004536 metric ton
1 short ton = 0.9072 metric ton
1 long ton = 2,240 pounds = 1.0160 metric tons

E. Energy (or Work) and Power

(Energy is the capacity for doing work. Power is the rate of doing work or the rate at which energy is supplied; power is energy per unit of time.)

a. Energy

1 gram-calorie = 0.003968 B.t.u.
1 gram-calorie = 3.091 foot-pounds
1 gram-calorie = 4.186 joules (watt-seconds)
1 kilogram-calorie = 3.968 B.t.u.
1 kilogram-calorie = 2.2046 pound-calories
1 pound-calorie = 1.8 B.t.u.
1 kilogram-meter = 7.233 foot-pounds
1 liter-atmosphere = 101.33 joules
1 kilogram-calorie = 0.001163 kilowatt-hour
1 kilogram-calorie = 0.00156 horsepower-hour
1 kilowatt-hour = 3,413 B.t.u.
1 B.t.u. = 252.0 gram-calories

1 foot-pound = 0.3235 gram-calorie
1 B.t.u. = 0.2520 kilogram-calorie
1 pound-caloric = 0.4536 kilogram-calorie
1 B.t.u. = 0.5555 pound-calorie
1 foot-pound = 0.1383 kilogram-meter
1 joule (watt-second) = 0.2389 gram-calorie
1 joule = 0.00986 liter-atmosphere
1 kilowatt-hour = 860.0 kilogram-calories
1 horsepower-hour = 641.8 kilogram-calories
1 B.t.u. = 0.000293 kilowatt-hour

b. Power

1 watt = 44.24 foot-pounds per minute
1 gram-calorie per second = 4.186 watts
1 kilowatt = 102.0 kilogram-meters per second
1 kilowatt = 738 foot-pounds per second
1 horsepower = 550 foot-pounds per second
1 horsepower = 42.44 B.t.u. per minute
1 kilowatt = 1.341 horsepower
1 kilowatt = 860 kilogram-calories per hour
1 boiler horsepower evaporates 34.5 lb of water per hour from and at 212°F.
1 boiler horsepower = 558.0 B.t.u. per minute = 140.7 kilogram-calories per minute.
1 foot-pound per minute = 0.0226 watt
1 watt = 0.2389 gram-calorie per second
1 kilogram-meter per second = 0.00980 kilowatt
1 foot-pound per second = 0.00136 kilowatt
1 foot-pound per second = 0.00182 horsepower
1 B.t.u. per minute = 0.02356 horsepower
1 horsepower = 0.746 kilowatt
1 kilogram-calorie per hour = 0.001163 kilowatt

F. Miscellaneous

1 atmosphere pressure = 760 millimeters of mercury
= 29.92 inches of mercury
= 33.90 feet of water
= 14.696 pounds per square inch
= 10,333 kilograms per square meter
1 gram per cubic centimeter = 62.4 pounds per cubic foot (weight of water)
1 gram weight = 981 dynes
1 B.t.u. per cubic foot = 8.900 kilogram-calories per cubic meter
1 B.t.u. per pound = 0.555 kilogram-calorie per kilogram
1 faraday = 96,494 coulombs
Electrochemical equivalent of silver = 0.001118 gram per second per ampere
1 volt = 23,060 gram-calories per gram equivalent in electrolysis
Volume of 1 gram-mol of gas at 0°C., 1 atmosphere pressure = 22.4146 liters
Volume of 1 pound-mol of gas at 32°F., 1 atmosphere pressure = 359.0 cubic feet
Volume of 1 pound-mol of gas at 60°F., 30 inches of mercury = 378.4 cubic feet
Value of gas constant (R) per gram-mol = 0.08207 liter-atmosphere per degree centigrade = 1.987 calories per degree centigrade
Value of gas constant (R) per pound-mol = 10.71 pounds per square inch × cubic feet per degree Fahrenheit = 1.987 B.t.u. per degree Fahrenheit
Acceleration of gravity (45° latitude at sea level) = 980.6 centimeters per second per second = 32.17 feet per second per second

TABLE LV.—INTERCONVERSION TABLES FOR UNITS OF VOLUME AND WEIGHT, AND ENERGY[1]

To convert from	Multiply by														
	To cubic inch	To cubic foot	To cubic yard	To fluid ounce	To pint	To quart	To gallon	To grain	To ounce (troy)	To ounce (avoir.)	To pound (troy)	To pound (avoir.)	To c.c. or gram	To liter or kilogram	To cubic meter
Cubic inch	1.0000	0.0_3579	0.0_4214	0.554112	0.03463	0.01732	0.00433	252.89	0.52686	0.57804	0.04390	0.03613	16.387	0.01639	0.0_4164
Cubic foot	1728.0	1.0000	0.03704	957.505	59.844	29.922	7.4805	437000	910.41	998.85	75.867	62.428	28317	28.317	0.02832
Cubic yard	46656.0	27.000	1.0000	25852.6	1615.8	807.90	201.97	117990_3	24581	26969	2048.4	1685.6	764556	764.56	0.76456
Fluid ounce	1.8047	0.00104	0.0_4387	1.00000	0.06250	0.03125	0.00781	456.39	0.95081	1.0432	0.07923	0.06520	29.574	0.02957	0.0_4296
Pint	28.875	0.01671	0.0_3619	16.0000	1.0000	0.50000	0.12500	7302.2	15.213	16.691	1.2677	1.0432	473.18	0.47318	0.0_4473
Quart	57.750	0.03342	0.00124	32.0000	2.0000	1.0000	0.25000	1460.4	30.426	33.382	2.5355	2.0863	946.35	0.94635	0.0_3946
Gallon	231.00	0.13368	0.00495	128.000	8.0000	4.0000	1.0000	58418	121.70	133.53	10.142	8.3454	3785.4	3.7854	0.00378
Grain	0.00395	0.0_5229	0.0_7847	0.002191	0.0_3137	0.0_4685	0.0_4171	1.0000	0.00208	0.00229	0.0_3174	0.0_3143	0.06480	0.0_4648	0.0_7648
Ounce (troy)	1.8980	0.00110	0.0_4407	1.05173	0.06573	0.03287	0.00822	480.00	1.0000	1.0971	0.08333	0.06857	31.103	0.03110	0.0_4311
Ounce (avoirdupois)	1.7300	0.00100	0.0_4371	0.958608	0.05991	0.02996	0.00749	437.50	0.91146	1.0000	0.07595	0.06250	28.350	0.02835	0.0_4283
Pound (troy)	22.777	0.01318	0.0_3488	12.6208	0.78880	0.39440	0.09860	5760.0	12.000	13.166	1.0000	0.82286	373.24	0.37324	0.0_3373
Pound (avoirdupois)	27.680	0.01602	0.0_3593	15.3378	0.95861	0.47931	0.11983	7000.0	14.583	16.000	1.2153	1.0000	453.59	0.45359	0.0_3454
C.c. or gram	0.06102	0.0_4353	0.0_5131	0.033814	0.00211	0.00106	0.0_3264	15.432	0.03215	0.03527	0.00268	0.00220	1.0000	0.00100	0.0_51
Liter or kilogram	61.024	0.03531	0.00131	33.8140	2.1134	1.0567	0 26417	15432	32.151	35.274	2 6792	2.2046	1000.0	1.0000	0.00100
Cubic meter	61024	35.315	1 308	33814 0	2113 4	1056 7	264 17	154320_3	32151	35274	2679.2	2204.6	10_6	1000 0	1 0000

NOTE: The small subnumeral following a zero indicates that the zero is to be taken that number of times; thus, 0.0_31428 is equivalent to 0.0001428. When volume and weight interconversions are given, water is the medium the calculations are based upon.

Table LV.—Interconversion Tables for Units of Volume and Weight, and Energy.[1]—(*Concluded*)

To convert from	Multiply by										
	To B.t.u.	To pound-calories	To kilogram-calories	To foot-pounds	To foot-tons	To kilogram-meters	To horse-power hours	To kilowatt-hours	To joules	To pounds C	To pounds H_2O
B.t.u.	1.0000	0.55556	0.25200	778.00	0.38900	107.56	0.0_3393	0.0_3293	1054.9	0.0_46859	0.00103
Pound-calories	1.8000	1.0000	0.45359	1400.4	0.70020	193.61	0.0_3707	0.0_3528	1898.8	0.0_31235	0.00185
Kilogram-calories	3.9683	2.2046	1.0000	3091.4	1.5437	426.84	0.00156	0.00116	4186.1	0.0_32722	0.00409
Foot-pounds	0.00128	0.0_3714	0.0_3324	1.0000	0.00050	0.13825	0.0_6505	0.0_6377	1.3562	0.0_78818	0.0_5132
Foot-tons	2.5707	1.4282	0.64780	2000.0	1.0000	276.51	0.00101	0.0_3753	2712.6	0.0_31762	0.00265
Kilogram-meters	0.00930	0.00516	0.00234	7.2330	0.00362	1.0000	0.0_5365	0.0_5272	9.8101	0.0_66336	0.0_5958
Horsepower-hours	2545.0	1413.9	641.33	1980000	990.00	273750	1.0000	0.74600	2685470	0.1746	2.6226
Kilowatt-hours	3412.7	1896.0	860.00	2654200	1327.1	366960	1.3404	1.0000	3599890	0.23400	3.5156
Joules	0.0_3948	0.0_3526	0.0_3239	0.73731	0.0_3369	0.10194	0.0_6372	0.0_6278	1.0000	0.0_76500	0.0_6977
Pounds C	14580	8100	3674	113430_3	5676	1568300	5.7284	4.2733	153850_3	1.00000	15.024
Pounds H_2O	970.40	539.11	244.54	754970	377.49	104380	0.38127	0.28442	1023970	0.06655	1.0000

The ton used is 2,000 lb "Pounds C" refers to pounds of carbon oxidized, 100 per cent efficiency, equivalent to the corresponding number of heat units. "Pounds H_2O" refers to pounds of water evaporated at 100°C = 212°F. at 100 per cent efficiency.

[1] Courtesy of Engineering Department, E. I. du Pont de Nemours & Company, Wilmington, Del.

TABLE LVI.—TEMPERATURE CONVERSION

°C.	°F.	°C.	°F	°C.	°F.	°C.	°F.	°C	°F.
-273	-459	400	752	1000	1832	1600	2912	-268	-450
-250	-418	410	770	1010	1850	1610	2930	-240	-400
-200	-328	420	788	1020	1868	1620	2948	-212	-350
-150	-238	430	806	1030	1886	1630	2966	-184	-300
-100	-148	440	824	1040	1904	1640	2984	-157	-250
-50	-58	450	842	1050	1922	1650	3002	-129	-200
-40	-40	460	860	1060	1940	1660	3020	-101	-150
-30	-22	470	878	1070	1958	1670	3038	-73	-100
-20	-4	480	896	1080	1976	1680	3056	-46	-50
-10	+14	490	914	1090	1994	1690	3074	-40	-40
0	32	500	932	1100	2012	1700	3092	-34	-30
5	41	510	950	1110	2030	1710	3110	-29	-20
10	50	520	968	1120	2048	1720	3128	-23	-10
15	59	530	986	1130	2066	1730	3146	-18	0
20	68	540	1004	1140	2084	1740	3164	-15	5
25	77	550	1022	1150	2102	1750	3182	-12	10
30	86	560	1040	1160	2120	1760	3200	-9	15
35	95	570	1058	1170	2138	1770	3218	-7	20
40	104	580	1076	1180	2156	1780	3236	-4	25
45	113	590	1094	1190	2174	1790	3254	-1	30
50	122	600	1112	1200	2192	1800	3272	+2	35
55	131	610	1130	1210	2210	1810	3290	4	40
60	140	620	1148	1220	2228	1820	3308	7	45
65	149	630	1166	1230	2246	1830	3326	10	50
70	158	640	1184	1240	2264	1840	3344	13	55
75	167	650	1202	1250	2282	1850	3362	16	60
80	176	660	1220	1260	2300	1860	3380	18	65
85	185	670	1238	1270	2318	1870	3398	21	70
90	194	680	1256	1280	2336	1880	3416	24	75
95	203	690	1274	1290	2354	1890	3434	27	80
100	212	700	1292	1300	2372	1900	3452	29	85
110	230	710	1310	1310	2390	1910	3470	32	90
120	248	720	1328	1320	2408	1920	3488	35	95
130	266	730	1346	1330	2426	1930	3506	38	100
140	284	740	1364	1340	2444	1940	3524	43	110
150	302	750	1382	1350	2462	1950	3542	49	120
160	320	760	1400	1360	2480	1960	3560	54	130
170	338	770	1418	1370	2498	1970	3578	60	140
180	356	780	1436	1380	2516	1980	3596	65	150
190	374	790	1454	1390	2534	1990	3614	71	160
200	392	800	1472	1400	2552	2000	3632	76	170
210	410	810	1490	1410	2570	2050	3722	83	180
220	428	820	1508	1420	2588	2100	3812	88	190
230	446	830	1526	1430	2606	2150	3902	93	200
240	464	840	1544	1440	2624	2200	3992	121	250
250	482	850	1562	1450	2642	2250	4082	149	300
260	500	860	1580	1460	2660	2300	4172	177	350
270	518	870	1598	1470	2678	2350	4262	204	400
280	536	880	1616	1480	2696	2400	4352	232	450
290	554	890	1634	1490	2714	2450	4442	260	500
300	572	900	1652	1500	2732	2500	4532	288	550
310	590	910	1670	1510	2750	2550	4622	316	600
320	608	920	1688	1520	2768	2600	4712	343	650
330	626	930	1706	1530	2786	2650	4802	371	700
340	644	940	1724	1540	2804	2700	4892	399	750
350	662	950	1742	1550	2822	2750	4982	427	800
360	680	960	1760	1560	2840	2800	5072	454	850
370	698	970	1778	1570	2858	2850	5162	482	900
380	716	980	1796	1580	2876	2900	5252	510	950
390	734	990	1814	1590	2894	3000	5432	538	1000

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